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Organic biomarkers in deep-sea regions affected by bottom trawling: pigments, fatty acids, amino acids and carbohydrates in surface sediments from the La Fonera (Palamós) Canyon, NW Mediterranean Sea

E. Sañé, J. Martín, P. Puig, and A. Palanques

Institut de Ciències del Mar, CSIC. Passeig Marítim de la Barceloneta, 37–49, 08003 Barcelona, Spain

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Correspondence to: E. Sañé (sane@icm.csic.es)

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Abstract

Deep-sea ecosystems are in general adapted to a limited variability of physical conditions, resulting in high vulnerability and slow recovery rates from anthropogenic perturbations such as bottom trawling. Commercial trawling is the most recurrent and pervasive of human impacts on the deep-sea floor, but studies on its consequences on the biogeochemistry of deep-sea sediments are still scarce. Pigments, fatty acids, amino acids and carbohydrates were analyzed in sediments from the flanks of the La Fonera (Palamós) submarine canyon (NW Mediterranean Sea), where a commercial bottom trawling fishery has been active for more than 70 yr. More specifically, we investigated how trawling-induced sediment reworking affects the quality of sedimentary organic matter which reaches the seafloor and accumulates in the sediment column, which is fundamental for the development of benthic communities. Sediment samples were collected during two oceanographic cruises in spring and autumn 2011. The sampled sites included trawl fishing grounds as well as pristine (control) areas. We report that bottom trawling in the flanks of the La Fonera Canyon has caused an alteration of the quality of the organic matter accumulated in the upper 5 cm of the seafloor. The use of a wide pool of biochemical tracers characterized by different reactivity to degradation allowed us to discriminate the long-term effects of trawled-induced sediment reworking from the natural variability caused by the seasonal cycle of production and sinking of biogenic particles. Differences between untrawled and trawled areas were evidenced by labile amino acids, while differences between spring and autumn samples were detected only by the more labile indicators chlorophyll *a* and mono-unsaturated fatty acids. These results suggest that changes in the biochemical composition of the sedimentary organic matter caused by bottom trawling can be more relevant than those associated with natural seasonality and pose serious concerns about the ecological sustainability of deep-sea trawling activities.

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1 Introduction

Commercial bottom trawling is a fishing activity that consists in pulling heavy fishing gears over the seafloor, with negative effects on the sedentary macrofauna and on fish-stocks (McConnaughey et al., 2000; Morato et al., 2006). Over the last decades, this commercial activity has been extending its operations over larger and deeper areas of the world oceans (Bensch et al., 2009). It has been recently estimated that the overall oceans' area (including continental shelf regions and seamounts) used as trawling grounds accounts for 20 million km^2, of which about one fourth is located on the continental slope at depths ranging 200–800 m (Puig et al., 2012). Due to their low resilience, deep sea areas (> 200 m) are more vulnerable to anthropogenic disturbance than shallow high-energy environments (Collie et al., 2000; McConnaughey et al., 2000) and, for this reason, the effects of bottom trawling on the deep benthic communities and their habitats need to be studied carefully.

Submarine canyons are morphological incisions traversing continental margins that have the capacity to facilitate the transport of dissolved and particulate matter from continental shelves to deeper waters (Granata et al., 1999; Allen and Durrieu de Madron, 2009; Palanques et al., 2011), and therefore, are sites of high productivity and organic matter enrichment (Vetter and Dayton, 1999; García and Thomsen, 2008; De Leo et al., 2010), where benthic communities are favoured by food availability. Not surprisingly, submarine canyons harbour valuable stocks of living resources and their surroundings are often targeted by commercial fisheries including bottom trawling (Company et al., 2012).

This study focuses on the flanks of the La Fonera Canyon (also known as Palamós Canyon), where a monospecific otter trawl fishery targeting the deep water shrimp *Aristeus antennatus* has been active for more than 70 yr to depths up to 800 m (Tobar and Sardà, 1987). Previous studies have shown that bottom trawling along the flanks of the La Fonera Canyon can trigger sediment gravity flows (Palanques et al., 2006), which transport sediments downslope from the fishing grounds into the canyon axis

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(Martín et al., 2006, 2007), affecting sediment accumulation rates in the lower canyon (Martín et al., 2008) and ultimately altering the morphology of the canyon flanks as a result of chronic reworking and removal of sediments (Puig et al., 2012).

This work aims to assess the effects of bottom trawling on the quality of the organic matter in surface sediments, by comparing regions affected and unaffected by this fishing technique. The quantity and the quality of the organic matter settling on the seabed represent the principal factors regulating benthic biomass (Grebmeier et al., 1988) and are important for the development of benthic communities (Thompson and Nichols, 1988; Graf, 1989). Organic matter indicators have been already used in other works, addressing the biochemical composition of sediments in submarine canyons (García and Thomsen, 2008; Pusceddu et al., 2010; Pasqual et al., 2011). Here, we utilized a pool of four biomarkers characterized by different susceptibilities to environmental conditions. Pigments and unsaturated fatty acids, the most labile compounds (Haddad et al., 1992; Wakeham et al., 1997), are good indicators of fresh organic matter, whereas carbohydrates are considered the most refractory macromolecules (Wakeham et al., 1997). Protein and neutral amino acids are less labile than pigments and unsaturated fatty acids, but, like them, are utilized as indicators of labile material (Lee et al., 2004). The use of this combination of biomarkers will allow us to study the effects of sediment reworking by trawling on the quality of the organic matter and also to compare them with those related to seasonal variability, being that sediment samples were collected both in spring and in autumn.

2 Materials and methods

2.1 Sampling

Coring stations were chosen based on previous knowledge on the distribution of fishing grounds in the La Fonera Canyon (Palanques et al., 2006). Trawling activities are conducted on the flanks of the canyon between 350 and 800 m depth along two main

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fishing grounds: Sant Sebastià on the northern flank and Rostoll on the southern flank (Fig. 1). The offshore sector of the southern flank remains unexploited by the trawling fleet and therefore will be used as a control site. The distribution of pristine and impacted areas schematized in Fig. 1 has been recently confirmed by means of satellite-based navigation tracks of fishing

vessels, high-resolution acoustic data and ROV observations showing that trawled areas present smoother morphologies at large spatial scales owing to the persistent disturbance of the seafloor by bottom fishing gears (Puig et al., 2012).

Samples were taken on board R/V *García del Cid* during two oceanographic cruises, *HERMIONE I*, in spring 2011 (SPR) and *HERMIONE II*, in autumn 2011 (AUTM). Station names, depths, coordinates and sampling dates are listed in Table 1 (see also Fig. 1). Two regions were targeted in the study area: an untrawled region in the offshore southern canyon flank (UTR, stations SF-3, SF-4, SF-5 and SF-6) and a trawled region comprising both the northern canyon flank and the inshore southern flank (TR: stations NF-1, NF-2, NF-3, NF-4, NF-5, NF-6, SF-1 and SF-2). All sampling stations were located within a water depth range of approximately 450–600 m. Sediment samples were taken using a KC multi-corer equipped with 6 polycarbonate tubes with an inner diameter (i.d.) of 9.4 cm. From each station, a tube with an undisturbed sediment-water interface was selected for analysis. During the SPR cruise, the multi-corer tubes were sub-sampled down to 5 cm with smaller tubes (i.d. 3.5 cm) that were immediately frozen at −20 °C. During the AUTM cruise, the multi-corer tubes were directly sub-sampled onboard in 1 cm slices from the top to 5 cm depth and subsamples were stored in plastic bags at −20 °C.

Except for the offshore part of the northern canyon flank (NF-5 and NF-6), the top 5 cm of the sediment column at sampled sites was basically composed of silty mud with variable amounts of sand (1–14 %) (Martín et al., 2012). We noticed that along the northern canyon flank the coarseness of topmost sediments and the stiffness of the muddy sediments below increased seawards. As a consequence, the multi-corer could not penetrate the seafloor at stations NF-5 and NF-6, although station NF-5 could be

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sampled with a box-corer that was available on board during the HERMIONE I cruise. Given the wide differences in both the sampling technique and the textural properties compared with all the other stations, the station NF-5 will be thereafter discarded for statistical analysis.

2.2 Laboratory analysis

Frozen sediment samples were freeze-dried (P = 0.1 mbar and T = −80 °C) for 24 h and prepared to be analyzed by High Performance Liquid Chromatography (HPLC) (pigments, amino acids and carbohydrates) or Gas Chromatography (GC) (fatty acids). The SPR surface sediment samples kept in the small tubes were subsampled at 1 cm intervals down to 5 cm to have the same vertical resolution as the AUTM sediment samples. Laboratory analyses were carried out on all single samples from 0 to 5 cm depth, although for some analyses there was not enough material left from specific centimetres.

2.2.1 Pigments

Pigments were extracted from sediments using the methodology described by Sun et al. (1991) and analyzed by HPLC following the protocol detailed by Wright et al. (1991). For each sample, pigments were extracted from sediments by adding 3 mL of pure acetone to approximately 2 g of freeze-dried sediment. After vortex mixing, samples were placed in an ultrasonic bath for 10 min and then centrifuged at 3000 rpm during 10 min. After recovering 1.5 mL of the supernatant, the entire procedure was repeated a second time in order to obtain for each sample approximately 3 mL of extract. Finally, the pigment extracts were evaporated with nitrogen, re-diluted with 200 µL of pure acetone, filtered with syringe nylon filters (pore diameter 0.45 µm) and transferred to HPLC vials for their later analysis.

Pigments were analyzed with a W-600 Controller coupled with a W717 autosampler using the technique HPLC-FP-diode array detector (DAD) (Gradient). The column was

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a C_{18} Prontosil-AA-FMOC 5 µm (250 × 4 mm). A Waters DAD 2996 (436 nm) and a Jasco FP-1520 (Ex. 440 nm, Em. 660 nm) were used as detectors. The mobile phase consisted in three solutions, (a) (methanol and ammonium acetate 0.5 M, 4 : 1 *v*/*v*), (b)(acetonitrile and Milli-Q water, 9 : 1 *v*/*v*) and (c) (ethyl acetate, HPLC grade). The velocity of the flux was 0.9 mL min^{-1} and the pressure 2500 psi. The volume of injection was 100 µL and the run time 34 min. The gradient is described in Wright et al. (1991). A mixed pigments standard (DHI) was also analyzed. Pigment peaks were identified in the chromatogram using the Empower Software, specific for the treatment of chromatographic data. Pigments were identified by knowing their retention times in the column and the wave length of maximum absorbance characteristic for each pigment.

Among pigments, chlorophyll *a* (Chl *a*) was used as an indicator of labile organic matter, whereas carotenoids (peridin, fucoxanthin, diatoxanthin, lutein, zeaxanthin and canthaxanthin) were used as refractory organic matter indicators. The Chl *a* to pheophytin *a* (Pheo *a*) ratio and the sum of the Chl *a* degradation products (pheophytin *a*, pheophorbide *a* and pyropheophorbide *a*) were used as degradation indexes.

Pigment relative abundances are expressed as percentages.

2.2.2 Fatty acids

Fatty acids (FA) were extracted through a one step transesterification process (Lewis et al., 2000; Christie, 2003; Indarti et al., 2005). Approximately 2 g of freeze-dried sediment were extracted in 8 mL of a cold solution of methanol, 98 % sulphuric acid and chloroform, in the presence of butyl hydroxytoluene (BHT), an antioxidant at a concentration of 50 mg L^{-1}. The ratio of methanol to chloroform to sulphuric acid in the solvent extraction was 1.7 : 2 : 0.3 *v*/*v*/*v*. After adding 20 µL of the internal standard nonadecanoic acid (1 mg mL^{-1}), samples were placed in a preheated oven (at 90 °C for 90 min) for lipids extraction and methylation of the released fatty acids in fatty acid methyl esters (FAME). Ultra pure water (2 mL) was added to each sample to partition the extract in two phases. Following centrifugation (5 min at 1500 rpm and 4 °C), the inferior chloroform phase was recovered. A second extraction was made with a solution

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of hexane and chloroform (4:1 v/v) and, after centrifugation (5 min at 1500 rpm and 4 °C), the superior phase was recovered and added to the first organic phase. This procedure was repeated twice. The organic phases were pooled and cleaned with a cold solution of potassium carbonate (2 %). After centrifugation (5 min at 1500 rpm and 4 °C), the organic phase was recovered, evaporated to dryness at room temperature, and diluted again with 400 µL of pure hexane prior to analysis.

FAME were analysed with a GC coupled to an ion-trap mass spectrometer (MS) GCMS-QP2010. A BPX70 chromatographic column was used. The column had a length of 30 m and an internal diameter of 0.25 mm; film thickness was 0.25 µm. The flow was constant with a velocity of 1 mL min^{-1}. The injector temperature was set to 260 °C and the volume injected was 1 µL. The use of known standards as reference (Supelco 37 Component FAME Mix) allowed FA quantification. Data were treated with the GCMSsolution Software version 2.5. The peaks of the chromatogram were identified based on FA molecular weights and on their retention times in the chromatographic column.

In order to present the dataset in a comprehensible form, fatty acids were grouped according to their chemical structure in: (a) polyunsaturated fatty acids (PUFA): compounds with two or more unsaturated bonds, (b) monounsaturated fatty acids (MUFA): compounds with one unsaturation, (c) mid chain fatty acids (MC-FA): chain length ≤ C_{20} and (d) long chain fatty acids (LC-FA): chain length C_{21}–C_{26}.

Concentrations are expressed in mg kg^{-1} DW.

2.2.3 Amino acids

Total hydrolysable amino acids (THAA) were analyzed following the AccQ-Tag method by Waters which utilizes the pre-column derivatization reagent 6-aminoquinolyl-N-hydroxysuccinimidyl carbamate (AQC) to produce fluorescently labelled amino acids for analysis. The Waters AccQ-Tag Fluor derivatization Reagent kit, ref: WAT52880 was used. Approximately 15 mg of freeze-dried sediment were submitted to hydrolysis with 250 µL of hydrochloric acid 12 N and 230 µL of Milli-Q water at 100 °C, during 24 h and

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under vacuum. Together with sediment samples, also the internal standard α-amino-n-butyric acid (AABA) was submitted to acidic hydrolysis. After the evaporation of the hydrolysate with a rotary evaporator, samples were derivatizated. The hydrolysate was redisolved with 300 µL of hydrochloric acid 20 mM, filtered with syringe nylon filters (pore diameter 0.45 µm) and buffered with 70 µL of a borax buffer solution. The reagent A (20 µL) was then added. After 1 min at ambient temperature and 10 minutes at 55 °C, the solution was mixed with 100 µL of the mobile phase and transferred to HPLC vials.

Analyses were carried out with a gradient HPLC Waters 600 coupled with a Waters Delta 600 pump and a Waters 2487 (Dual Absorbance Detector) UV absorption detector (Ex. 250 nm, Em. 395 nm). The column was a NOVA-PAK® C_{18} 4 µm 3.9 × 150 mm Part No WAT086344. An automatic injector Waters 717 plus and an In-Line Degasser AF were utilized. Analyses were carried out at a temperature of 37 °C. The mobile phase consisted in three solutions, (a) (AccQ-Tag Eluent A), (b)(acetonitrile) and (c)(HPLC grade water). The velocity of the flux was 1 mL min^{-1} and the pressure 2000 psi. The volume of injection was 20 µL and the run time 55 min. The Pierce (Thermo Scientific) Amino Acid Standard H, 10 × 1 mL (reference 200880) was used.

Data were treated with the JASCO ChromPass Chromatography Data System Software version 1.7.403.1. Two sub-groups of THAA, neutral THAA (alanine, valine, isoleucine, leucine and phenylalanine) and protein THAA (aspartic acid, serine, glutamic acid, glycine, histidine, arginine, threonine, alanine, tyrosine, valine, lysine, isoleucine, leucine and phenylalanine) were used as labile organic matter indicators. The aspartic acid (Asp) to β-alanine (BALA) and the glutamic acid (Glu) to γ-aminobutyric acid (GABA) ratios were utilized as degradation indexes.

Concentrations are expressed in nmol mg^{-1} DW.

2.2.4 Carbohydrates

For the analysis of carbohydrates (CHO), sediment samples were prepared following the protocol of Oakes et al. (2010). A volume of 0.5 mL of concentrated (11 M) sulphuric

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acid was added to approximately 0.5 g of freeze-dried sediment. The mixture of sediment and sulphuric acid was mixed with the vortex and, after one hour, 4.5 mL of Milli-Q water were added to reduce the concentration of sulphuric acid from 11 to 1 M. Samples were then hydrolysed during 1 h at 120 °C (the reaction was stopped by placing on ice the Corning Pyrex glass tubes containing the samples). After neutralization with approximately 2 g of strontium carbonate and centrifugation (15 min at 15 000 rpm), the hydrolysate was transferred to Eppendorf tubes and stored overnight at −20 °C. Before preparing the HPLC vials, Eppendorf tubes were centrifuged again (15 min at 15 000 rpm) and the supernatant was filtered with syringe nylon filters (pore diameter 0.45 µm).

Carbohydrates were analyzed with a Waters 2695 52C Separations module chromatograph coupled with a Waters 2414 Refractive Index detector (temperature 37 °C and sensitivity 16). Two columns were utilized, an Aminex HPX-87P (300 × 7.8 mm) and an Aminex HPX-87C (300 × 7.8 mm). The mobile phase consisted in Milli-Q water. The velocity of the flux was 0.6 mL min^{-1} and the pressure 1700 psi. The volume of injection was 100 µL and the run time 25 min. Standard reagents of D(+)-Glucose Anhydrous (reference G-8270 Sigma), D(+)-Xylose (reference X1500 Sigma), D(+)-Galactose (reference G-0750 Sigma) and D(+)-Mannose (reference 63580 Fluka) were also analysed to obtain quantitative data. Carbohydrate peaks were identified in the chromatogram through their retention times, using the Empower Software, specific for the treatment of chromatographic data.

Due to the low quantity of sediment available from those stations sampled in spring, it has been possible to perform CHO analyses only on autumn samples.

Concentrations are expressed in mg g^{-1} DW.

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2.3 Statistics

Univariate and multivariate statistical tests were carried out on all the analyzed samples.

Univariate statistical analyses were performed with the Statistica software v.5.5. One-way ANOVA comparisons were made to test for differences between spring (SPR) and autumn (AUTM) and between the untrawled and the trawled regions (UTR and TR, respectively). Normality and homogeneity of variances were tested before performing the one-way ANOVA. Normality was assessed through the Kolmogorov-Smirnov (K-S) test. The null hypothesis of the K-S test is that no difference exists between the distribution of the data set and an ideal Gaussian distribution. When the p-value of the K-S test is lower than 0.05, the null hypothesis is rejected, meaning that the data did not follow a normal distribution. Measures of shape, like skewness and kurtosis, were also considered, being that a normal distribution is characterized by values of skewness comprised between −0.5 and 0.5 and values of kurtosis approximately equal to 3. When normality was violated, data were transformed before testing the homogeneity of variances (homoscedasticity). Homoscedasticity was tested though the Hartley's F_{max} test (Hartley, 1950), by dividing the larger variance by the smaller one to obtain the F-ratio. An F-ratio value close to 1, or higher than 1 but lower than the value in the F_{max} table, indicated homogeneity of variance. Since the number of samples was not the same within both the couple of groups compared, the degrees of freedom were calculated considering the higher number of samples for each couple of groups. When there was no normality and/or homogeneity of variance, a more conservative level of significance was considered ($p = 0.001$).

Multivariate statistical analyses were also performed. In this case, the Primer software v.6 was utilized (Clarke, 1993; Clarke and Gorley, 2006). Before multivariate analysis, data were pre-treated by a transformation to downweight contributions from quantitatively dominant macromolecules. Euclidean distances between couples of samples were then calculated to obtain a triangular distance matrix. Differences between SPR

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and AUTM and between UTR and TR were tested through the non-parametric analysis of similarities (ANOSIM test). ANOSIM is a resemblance-based permutation method used to test the null hypothesis of "no differences" between a priori defined groups of multivariate samples. Since dissimilarities are not normally distributed, ANOSIM uses ranks of pairwise dissimilarities. The null hypothesis is that the average of rank dissimilarities between objects within groups is equal to the average of rank dissimilarities between objects from different groups. The ANOSIM R statistic value is used to measure how different two groups are and it is calculated from the average of rank dissimilarities between objects (by subtracting the average of rank dissimilarities within groups to the average of rank dissimilarities between groups). When $R = 0$, inter- and intra-group differences are equal, when $R < 0$, intra-group differences are higher than inter-group differences, whereas when $R > 0$, inter-group differences are higher than intra-group differences (Clarke and Gorley, 2001).

The similarity percentages (SIMPER) test was carried out to quantify the contribution of biomarkers to dissimilarities within and between trawling regions and season groups. SIMPER uses the Bray-Curtis dissimilarity to calculate the percentage contribution of each variable (i.e. Chl *a*; MUFA: 16 : 1, 18 : 1t, 18 : 1, 18 : 1c, 20 : 1, 22 : 1, 24 : 1; protein and neutral THAA: Asp, Ser, Glu, Gly, His, Arg, Thr, Ala, Tyr, Val, Lys, Ile, Leu, Phe) to the dissimilarities within each a priori-defined group (i.e. UTR, TR, SPR and AUTMN), between trawling regions (UTR and TR) and between sampling seasons (SPR and AUTMN). The average square distance is shown together with the % contribution of each variable to the average square distance.

Principal components analysis (PCA) was used to identify the best biomarker (among Chl *a*, 16 : 1, 18 : 1t, 18 : 1, 18 : 1c, 20 : 1, 22 : 1, 24 : 1, Asp, Ser, Glu, Gly, His, Arg, Thr, Ala, Tyr, Val, Lys, Ile, Leu and Phe) to distinguish between trawling regions and between season groups. The PCA is a multivariate technique used to reduce the multi-dimensionality which corresponds to the variation of a high number of correlated variables. Multi-dimensionality is reduced to two or three dimensions which correspond to a limited number of uncorrelated components, each of which is a combination of the

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original variables. The extracted uncorrelated components are called principal components (PC) and are estimated from the correlation matrix of the original variables. The objective of PCA is to reduce dimensionality by extracting the smallest number of components that account for most of the variation in the original multivariate data and to summarize the data with no loss of information. The first PCA accounts for as much of the variation as possible and each successive component accounts for a little less. The eigenvalues measure the amount of the variation explained by each PC and will be largest for the first PC and smaller for the subsequent PCs, whereas the eigenvectors provide the weights to compute the uncorrelated PC.

3 Results

Laboratory analysis results are shown in Tables 2–5, whereas statistical test results are shown in Tables 6–8.

A significant difference between SPR and AUTM was found in the Chl *a* (SPR: 5.99 ± 5.93; AUTM: 1.84 ± 2.15) (Tables 2a and 7) and carotenoid (SPR: 13.47 ± 7.75; AUTM: 11.99 ± 7.44) (Tables 2c and 7) percentages and, as regards Chl *a* degradation products, in the sum of the percentages of the Chl *a* degradation products (SPR: 18.22 ± 11.61; AUTM: 23.97 ± 12.68) (Tables 2b and 7). The Chl *a* to Pheo *a* ratio also showed significant inter-seasonal differences (SPR: 1.60 ± 1.86; AUTM: 0.43 ± 0.82) (Table 6c), with a p-value of 0.004. Nevertheless, neither AUTM nor SPR samples showed a normal distribution (Table 6a), which is one of the assumptions for performing ANOVA. Therefore, an ANOVA p-value lower than the observed 0.004 (Table 6a) would have been preferable to consider the two groups significantly different.

The total concentration of FA varied from $\sim 1.4\,mg\,kg^{-1}$ DW (at NF-3 station, from 4 to 5 cm depth) to $\sim 43.1\,mg\,kg^{-1}$ DW (at SF-5 station, from 0 to 1 cm depth) (Table 3). PUFA and MC-FA concentrations were not significantly different neither between seasons nor between trawling regions. On the contrary, significant differences in MUFA concentrations were found both between SPR and AUTM (SPR: 6.97 ± 4.85; AUTM:

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1.48 ± 0.95) and between UTR and TR (UTR: 3.28 ± 3.58; TR: 2.94 ± 3.80) (Table 7). Finally, LC-FA concentrations were significantly different between sampling seasons (SPR: 2.68 ± 1.06; AUTM: 1.32 ± 0.67) and, in AUTM, also between trawling regions (UTR: 1.66 ± 0.81; TR: 1.05 ± 0.38) (Table 7).

The total concentration of THAA varied from ∼ 11 nmol mg^{-1} DW (at NF-4 station, from 3 to 4 cm depth) to ∼ 32 nmol mg^{-1} DW (at SF-3 station, from 2 to 3 cm depth) (Table 4). No significant differences in the concentration of total, protein and neutral THAA were found between SPR and AUTM. Significant differences between UTR and TR were found in the concentrations of total (UTR: 22.38 ± 3.44; TR: 16.57 ± 4.19), protein (UTR: 18.58 ± 3.33; TR: 13.28 ± 3.88) and neutral (UTR: 4.66 ± 0.68; TR: 3.09 ± 0.92) THAA (Table 7). No significant differences in the Asp to BALA and the Glu to GABA ratios were found between SPR and AUTM or between UTR and TR (Table 6c).

Carbohydrate results are shown in Table 5. The total concentration of carbohydrates varied from ∼ 0.3 mg g^{-1} DW (at SF-4 station, from 2 to 3 cm depth) to ∼ 1.1 mg g^{-1} DW (at SF-3 station, from 2 to 3 cm depth) (Table 5). A significant difference between UTR and TR was found for xylose (UTR: 0.11 ± 0.07 mg g^{-1} DW; TR: 0.07 ± 0.02 mg g^{-1} DW) but not for rhamnose or for the labile sugars glucose and mannose (Tablec 6c and 7). Nevertheless, xylose samples from the untrawled and the trawled regions did not show homogeneity of variance (Table 6b), which is one of the assumptions for using ANOVA. Therefore, like for the Chl *a* to Pheo *a* ratio, an ANOVA p-value lower than the observed 0.020 (Table 6c) would have been preferable to consider the two groups significantly different.

Based on the SIMPER analysis, homogeneity was similar in the untrawled and in the trawled region (average square distance: 15.62 and 19.79, respectively), and amino acids (total, protein and neutral THAA) contributed with low percentages to the average square distance within UTR and TR (Table 8a). Homogeneity was similar also in AUTM and in SPR (average square distance: 18.87 and 21.45, respectively), and, in both cases, Chl *a* and MUFA showed low contributions to the intra-group distances (Table 8a). Inter-group distances were higher than intra-group distances (Table 8a and b).

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Similar average square distances were found between UTR and TR (average square distance: 51.20) and between SPR and AUTM (average square distance: 51.67) (Table 8b). Based on the intra-group distances, as expected, amino acids contribute with high percentages to the average square distance between UTR and TR, whereas the contribution of Chl *a* and MUFA was high in the case of the seasonal inter-group distances (Table 8b).

Based on the PCA, PC1 accounts for the 45.5 % of the total variation and explains the distribution of total, protein and neutral THAA between trawling regions (Figs. 2a, 3a and b), whereas PC2 accounts for the 18.1 % of the total variation and explains the distribution of Chl *a* and MUFA between sampling seasons (Figs. 2b, 3c and d).

4 Discussion

The main objective of this study is to characterize the organic matter (OM) present in sediments from two regions of a submarine canyon affected and unaffected by bottom trawling. To reach this goal, four biomarker groups, pigments, fatty acids, amino acids and carbohydrates were analyzed. Each biomarker showed a different pattern of distribution in the study area and some biomarkers appeared more appropriate than others to trace the impact of trawling. In addition, the use of this pool of biomarkers allowed us to identify differences in the quality of the OM between spring and autumn samples.

It has to be considered first, that biogenic particles, after being synthesised in the euphotic zone of the water column, reach the seafloor often after adsorption onto ballast minerals, which increases the sinking velocities of the resulting organomineral aggregates reducing the partial degradation of the OM in its transit through the water column (Armstrong et al., 2002; Ploug et al., 2008; Kaiser and Benner, 2012). High sinking velocities favour, in fact, the preservation of the organic compounds making possible their use as sediment biomarkers. Once in the sediment column, OM preservation is controlled by several interrelated factors, like oxygen penetration, bioturbation, sediment density and grain size, among others. The monomeric components of biomolecules

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degrade at similar rates under oxic and anoxic conditions (Henrichs and Doyle, 1986), but macrobiomolecules degradation is faster in oxic conditions than in anoxic compact sediments where benthic organisms cannot survive and cannot participate, together with bacteria, to OM degradation (Sun et al., 1993). Thus, the anoxia related to sediment compactness increases OM preservation excluding the ingestion and bioturbation of sediments by the benthic animal community (Bianchi et al., 2000). Also protozoa, like benthic organisms, need oxygen to survive, contributing to the higher degradation rates measured in oxic than in anoxic sediments (Williams, 1981). The influence of sediment grain size on OM preservation has been studied by Mayer (1994), who suggested that OM particles are included in surface grain pores which are too small (< 10 nm width) to allow the action of hydrolytic enzymes. Due to the higher surface volume ratio of smaller than bigger sediment grains, OM preservation should be higher in fine than in coarse sediments.

It has been stated that bottom trawling affects the physical properties of the seafloor, altering grain-size distributions and sediment porosity (McConnaughey et al., 2000). In addition, the pulling of the bottom trawl gears along the seafloor is deemed responsible for surface sediment resuspension, which is in this way oxygenated and may lose its finest fraction (e.g. Palanques et al., 2001). By removing bioturbators and at the same time artificially mixing sediments, bottom fishing gear is expected to deeply affect benthic community composition and metabolism and hence the biogeochemical characteristics of the affected sediments (Duplisea et al., 2001). These environmental factors influence OM preservation and can be responsible for making trawling regions different in terms of the quality of the OM present in the sediment column.

4.1 Pigments

The distribution of chlorophyll *a* (Chl *a*) in SPR and AUTM samples (Figs. 2b and 3d) suggests that this pigment, which is present in all photosynthetic algae and higher plants, can be used as an indicator of the seasonal fresh OM input to the seafloor also in the trawled submarine canyon flanks. In spring, high percentages of Chl *a* were found

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not only at UTR but also at TR (Table 2a), indicating that the information associated to this tracer (presence of very fresh OM, Wakeham et al., 1997) is prevalent in all the study area and hence not masked by the long-terms effects of bottom trawling. This agrees with a previous work carried out in the south western canyons of the Gulf of Lion, in which high quantities of fresh organic matter were found in spring sediment trap samples (Pasqual et al., 2011). On the contrary, no significant differences in the Chl *a* percentage were observed between UTR and TR, even if looking separately at spring and autumn samples (Table 6c). The lack of significant differences in spring can not be related exclusively to the low number of samples available (15, in contrast with the 34 samples available for the autumn period), which is evidenced by the high p-value ($p = 0.306$). Due to the high value of the mean squares of the error (i.e. to the high intra variability), the F-value obtained with the statistical test one-way ANOVA (~ 1, see Table 6c) is lower than the critical value of the F for a significance level of 5 % (4.667), and the null hypothesis of equal Chl *a* percentages at UTR and TR cannot be rejected. Based on these results, we hypothesize sediments reworking by trawling to exert a deeper impact on OM degradation than seasonality and that the highly labile Chl *a* biomarker is useful to detect only the subtle OM quality differences between SPR and AUTM sediments and too sensitive to evidence alterations in the quality OM related to trawling activities.

Chl *a* is degraded to pheophytin *a* (Pheo *a*) by loss of the Mg, to pyropheophorbide *a* by loss of the Mg, the phytyl chain and the carbomethoxy, and to pheophorbide *a* by loss of the phytyl chain and oxidation (Louda et al., 2008). Chl *a* degradation products can be used as OM quality indicators (Lee et al., 2000), like the Chl *a* to Pheo *a* ratio and the sum of the Chl *a* degradation products (Lee et al., 2004). However, when using these pigment degradation indexes, it should be considered that the formation of such degradation products depends not only on those environmental factors which enhance Chl *a* degradation but also on the initial concentration of Chl *a*. Low percentages of pheophytin *a*, pyropheophorbide *a* and pheophorbide *a* can be related to Chl *a* preservation and/or to an initial low availability of Chl *a*. In spite of these considerations, the

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use as degradation indexes of the Chl *a* to Pheo *a* ratio and the sum of the Chl *a* degradation products confirmed the presence of fresher OM in spring than in autumn samples (Tables 6c and 7).

Another group of pigments is represented by carotenoids, which are characterized by a higher stability than chlorophylls (Reuss, 2005) and may represent the majority of pigments in sediment samples (Repeta and Gagosian, 1987). The distribution of carotenoid percentages suggested higher amounts of refractory OM in spring than in autumn (Tables 2c and 7). In the study area, the relevance of lateral transport of particulate matter (Martín et al., 2006) could mask the signal of the vertical deposition of refractory OM particles onto the seafloor. Labile compounds are also laterally transported, but since they degrade with time, once they settle on the seafloor it is possible to distinguish between the fresh forms, representative of the vertical component of the OM input, and the degraded forms, which are the result of degradation processes during lateral transport. In addition, the presence of carotenoids is not influenced by those environmental factors related to trawling or seasonality which influence the biochemical quality of sediments, therefore their distribution in the study area can not help us understanding the effects of these two external factors. For these reasons, not only carotenoids, but all refractory compounds are less adequate as biomarkers than labile compounds.

4.2 Fatty acids

Like Chl *a*, also the labile monounsaturated fatty acids (MUFA) indicated an efficient input of fresh OM (Haddad et al., 1992) to the seafloor following the spring phytoplankton bloom. The lack of significant differences in the concentration of polyunsaturated fatty acids (PUFA) between SPR and AUTM samples (Table 7) may be related to the low number of PUFA compounds found in the study area (only two: FA 22 : 2 and FA 22 : 6, see Table 3a), which indicates a rapid degradation of this labile group of FA before accumulating in the sediment column (Haddad et al., 1992; Sun and Wakeham, 1994). The degradation of FA, aliphatic hydrocarbon chains with a carboxylic group at

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one extremity, is selective and depends on the number of carbons and double bonds of the chain. PUFA, FA with a high number of double bonds, represent the most labile group of FA and their low concentration even in SPR, when high Chl *a* percentages and MUFA concentrations were found (Tables 2a and 3b), suggests a previous degradation in the water column and/or after deposition on the seafloor (Sun et al., 1997; Wakeham et al., 1997). The selective degradation of PUFA can be particularly intense at the sediment-water interface (Laureillard et al., 1997) and prevents their use as tracers of fresh OM in this region.

The distribution in the study area of MUFA recorded differences not only between SPR and AUTM, but also between trawling regions (Table 7). The higher MUFA values found at UTR than at TR suggest that sediment resuspension caused by bottom trawling probably increases the exposure of MUFA to oxygen, enhancing its degradation at TR. Both MUFA and Chl *a* were useful to detect the presence of fresh OM in spring samples (Figs. 2b and 3d), but only MUFA detected differences in the nutritional quality of the OM related to sediment reworking by trawling (Tables 6c and 7). Probably due to their lower susceptibility to degradation, MUFA compounds were more useful than Chl *a* to distinguish between the reworked TR sediments and the fresher sediments at UTR (Fig. 4). Nevertheless, the behaviour of the two biomarkers can be considered only slightly different since the "Global R" value of the ANOSIM multivariate statistical test evidenced considerably lower differences in the concentration of MUFA between UTR and TR than between SPR and AUTM (Table 7). The preservation of Chl *a* and MUFA in the study area allowed us to use them to trace minor differences between sampling seasons in the "freshness" of the OM. On the other side, these labile biomarkers, in particular Chl *a*, did not appear appropriate to distinguish between trawled and untrawled regions (Fig. 4).

Mid and long chain FA (MC-FA and LC-FA, respectively) represent the most refractory fatty acid groups. MC-FA did not evidence differences in the quality of the OM in the study area, neither between seasons nor between trawled/untrawled regions, whereas LC-FA evidenced seasonal differences and, in autumn, also differences between the

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untrawled and the trawled regions (Table 7). Nevertheless, the distribution of LC-FA in the study area suggested high quantities of refractory material in spring and in the untrawled region, letting us doubt again about the utility of refractory compounds (i.e. carotenoids, MC-FA and LC-FA) as biomarkers in the study area, also due to the considerable lateral component of particle fluxes (Martín et al., 2006).

To summarize, the fatty acid group includes compounds characterized by a wide range of different labilities. Depending on its lability, each compound behaves in a different way (Fig. 4). At the two extremes, the FA with highest (PUFA) and lowest lability (MC-FA and LC-FA) did not trace differences in the quality of the OM, neither between seasons nor between trawling regions. PUFA are too labile and probably degrade before accumulating in the sediment column, whereas MC-FA and LC-FA are too refractory to be used as biomarkers. MUFA are able to detect differences both between sampling seasons and trawling regions. Based on the multivariate statistical test ANOSIM (Table 7), these compounds are more useful to trace the subtle differences between SPR and AUTMN than those related to sediment reworking by trawling for which they may be considered too labile and therefore too sensitive.

4.3 Amino acids

Like the other macromolecules studied, also amino acids are partially degraded in the water column, but a fraction of the amino acid pool reaches the seafloor and is incorporated in the sediment column (Wakeham et al., 1997; Moore et al., 2012), allowing the use of these compounds as biomarkers of the quality of the OM. When compared with other results from the NW Mediterranean continental shelf at ~ 300 m depth (Grémare et al., 2002, 2005), THAA showed relatively high values in the study area, which can be related to the high downward particles fluxes measured in the canyon (Martín et al., 2006). Amino acids are also considered fresh OM indicators (Lee et al., 2004) and the distribution of THAA values in the study area, with higher mean concentrations in the control area (~ 22 ± 3 nmol mg^{-1} DW) than in the trawled area (~ 17 ± 4 nmol mg^{-1} DW), confirmed the presence of more labile material at UTR (Figs. 2a and 3a), as

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previously suggested by MUFA biomarkers. Statistical tests indicated a clear separation between trawled regions when using THAA as biomarkers, more evident than the separation observed with MUFA as tracers (Table 7). The presence of more labile OM in the untrawled than in the trawled region is evidenced also by the distribution of neutral and protein THAA (Figs. 2a and 3a). Neutral THAA are not adsorbed onto clay minerals and are more susceptible to degradation than charged ones. Regarding protein THAA, their concentrations depend on the phytoplanktonic production and, like neutral THAA, can be used as fresh OM indicators. Other THAA, like β-alanine (BALA) which origins from aspartic acid (Asp) and γ-aminobutyric acid (GABA) which origins from glutamic acid (Glu), are associated to degradation processes and may be used as degradation indexes (Ingalls et al., 2003), but the absence of significant differences in the Asp to BALA and Glu to GABA ratios between UTR and TR (Table 6c) supports the doubts expressed by other authors on the validity of these ratios as OM quality indicators (García and Thomsen, 2008). The different degradation pathways and/or rates of Asp and Glu to BALA and GABA, respectively, can be responsible for the inconsistence of the Asp to BALA and Glu to GABA ratios as organic matter degradation indexes (Lee et al., 2000).

Based on the distribution of THAA in the trawled areas, we might expect higher concentrations of neutral and protein THAA in SPR than in AUTM samples. Nevertheless, no differences were found in the distribution of these THAA indicators between spring and autumn sediments (Table 7). Amino acids are considered less susceptible to degradation than Chl *a* and MUFA (Wakeham et al., 1997) and this characteristic could make them less adequate than the other two biomarkers to trace seasonal differences in the nutritional quality of the sedimentary OM. As mentioned before, based on our results, we hypothesize differences in the "freshness" of the OM related to seasonality to be subtle and for this reason detectable by very labile and sensitive OM indicators like Chl *a* and MUFA but not by less reactive biomarkers like amino acids (Fig. 4).

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4.4 Carbohydrates

Among labile sugars, only xylose (Opsahl and Benner, 1999) showed a higher concentration at UTR than at TR (Table 6c), following the distribution pattern of the other fresh OM indicators studied (MUFA, neutral THAA and protein THAA) (Table 7). The absence of significant differences between UTR and TR in the concentration of other labile sugars like glucose (Hedges et al., 1988; Hofmann et al., 2009) and mannose (Kerhervé et al., 2002) (Table 7) can be related to the low lability of these compounds if compared with that of MUFA or THAA. In spite of the relative lability of xylose, glucose and mannose, CHO compounds are in fact considered macromolecules with a low nutritional quality (Handa and Tominaga, 1969), characteristic of regions where the supply of fresh OM is limited, like deep-sea habitats (Danovaro et al., 1993) and oligotrophic environments (Rodil et al., 2007), and more resistant to degradation than pigments, fatty acids and amino acids (Wakeham et al., 1997). Carbohydrates did not detect differences among trawled and control areas, confirming our idea about the utility of refractory compounds as tracers.

4.5 Organic matter differences between trawled and untrawled regions

As expected, environmental factors related to the resuspension of sediments caused by the passage of the bottom trawl gears, like sediments oxygenation and the loss of the sediments finest fraction, does not favour the preservation of the organic matter in the trawled region, making trawling regions different in terms of the quality of the organic matter present in the sediment column. Our hypothesis that fresher organic matter would be present in the untrawled rather than in the trawled region was confirmed. Nevertheless, as expected, only some of the four biomarkers analyzed provided a good evidence of this hypothesis. The best biomarker in this geographical region to trace the effects of sediments reworking by trawling on the biochemical quality of sediments was represented by amino acids. The higher concentrations of total, neutral and protein THAA found in the untrawled than in the trawled region were supported by multivariate

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statistical tests like ANOSIM and PCA (Figs. 2a and 3a). Amino acids appeared as good biomarkers to trace differences associated to sediment reworking, giving valuable information for future investigations on the effects of trawling in deep-sea sediments from areas characterized by similar environmental conditions.

The use of four groups of biomarkers differently susceptible to degradation also allowed us to have qualitative information about the potential effects of trawling on the quality of the OM. PUFA and CHO did not add information on the impact of trawling in comparison with that of seasonality because both compounds were not able to detect any differences related to these two external factors, the first for its high lability and the second for its low lability (Fig. 4). But the case of Chl *a*, MUFA and THAA is different. The similar behaviour of Chl *a* and MUFA, which appeared as good biomarkers for seasonality but too labile to trace differences in the quality of the OM related to long-term chronic perturbations such as bottom trawling, and the opposite behaviour of the less labile THAA, which appeared better suited to trace changes associated to trawling but were too refractory to trace differences related to seasonality, suggested that the impact exerted by trawling on the biochemical composition of sediments is higher than the natural variation related to seasonality (Fig. 4). Since deep-sea trawling is not exclusive of the study area but widely extended throughout the world oceans (Bensh et al., 2009; Puig et al., 2012), our results suggest that commercial bottom trawling may have produced changes in the nutritional quality of deep-sea sediments at large spatial scales.

5 Conclusions

Bottom trawling in the flanks of La Fonera Canyon has caused an alteration of the quality of the organic matter in surface sediments (upper 5 cm). This study allowed us to identify amino acids as the more appropriate biomarkers to trace differences associated to sediment reworking caused by repeated bottom trawling.

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Differences between spring and autumn sediments were detected by the most labile biomarkers, Chl *a* and MUFA (percentage contribution to the Average Square Distance between SPR and AUTM: > 4.5 %), without any significant difference between untrawled and trawled regions (percentage contribution of Chl *a* and MUFA to the Average Square Distance between UTR and TR: < 4.5 %).

The high percentage contribution to the Average Square Distance between SPR and AUTM for Chl *a* and MUFA together with the high percentage contribution to the Average Square Distance between UTR and TR for the majority of amino acids (> 4.7 %) suggest that alterations in the quality of the organic matter caused by trawling can be considered relatively high if compared with the effects of seasonality.

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Table 1. Names, depths, coordinates and sampling dates of the coring stations. Trawled (TR) and untrawled (UTR) regions as well as Spring (SPR) and Autumn (AUTM) sampling seasons corresponding to each station are also indicated.

Station	Depth (m)	Latitude° N (decimal)	Longitude° E (decimal)	Sampling date	Trawling region	Sampling season
NF-1	475	41.8853	3.3070	12 Oct 2011	TR	AUTM
NF-2	500	41.8860	3.3321	13 May 2011	TR	SPR
NF-3	591	41.8903	3.3495	12 Oct 2011	TR	AUTM
NF-4	486	41.8892	3.3785	12 Oct 2011	TR	AUTM
NF-5	556	41.8890	3.4093	12 May 2011	TR	SPR
NF-6	470	41.8978	3.4257	12 Oct 2011	TR	AUTM
SF-1	463	41.8512	3.2912	12 Oct 2011	TR	AUTM
SF-2	503	41.8340	3.3178	13 May 2011	TR	SPR
SF-3	457	41.8150	3.3433	12 Oct 2011	UTR	AUTM
SF-4	453	41.8102	3.3652	11 Oct 2011	UTR	AUTM
SF-5	472	41.8075	3.3872	13 May 2011	UTR	SPR
SF-6	498	41.7942	3.4075	11 Oct 2011	UTR	AUTM

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Table 2. Pigment results (only percentages of the identified pigments are shown). (Abbreviations: Chl *a*, chlorophyll *a*; Pheo *a*, pheophytin *a*; Pheoph *a*, pheophorbide *a*; Pyropheoph *a*, pyropheophorbide *a*; Fucox, fucoxanthin; Diatox, diatoxanthin; Zeax, zeaxanthin; Canthax, canthaxanthin). The only station sampled with a box-corer, NF-5, is marked in dark grey. No sediment was available for the following sample: SF-4, from 0 to 1 cm.

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Table 2a. Chlorophyll.

Station	Core depth (cm)	Chlorophyll % Chl *a*
NF-1	0–1	0.00
	1–2	0.00
	2–3	0.00
	3–4	1.26
	4–5	0.00
NF-2	0–1	12.27
	1–2	13.14
	2–3	6.85
	3–4	0.00
	4–5	11.54
NF-3	0–1	1.54
	1–2	0.00
	2–3	3.75
	3–4	0.00
	4–5	5.3
NF-4	0–1	7.07
	1–2	1.56
	2–3	0.00
	3–4	6.42
	4–5	4.11
NF-5	0–1	3.99
	1–2	2.75
	2–3	4.67
	3–4	1.03
	4–5	7.05
SF-1	0–1	3.18
	1–2	0.00
	2–3	3.50
	3–4	0.00
	4–5	0.00
SF-2	0–1	0.00
	1–2	17.24
	2–3	0.00
	3–4	0.00
	4–5	10.34
SF-3	0–1	1.56
	1–2	2.42
	2–3	0.37
	3–4	5.39
	4–5	3.08
SF-4	1–2	0.99
	2–3	0.00
	3–4	1.43
	4–5	4.84
SF-5	0–1	1.63
	1–2	7.80
	2–3	7.61
	3–4	1.41
	4–5	0.00
SF-6	0–1	0.00
	1–2	0.00
	2–3	0.00
	3–4	3.90
	4–5	0.92

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Table 2b. Chlorophyll *a* degration products.

Station	Core depth (cm)	Chlorophyll Degradation Products		
		% Pheo *a*	% Pheoph *a*	% Pyropheoph *a*
NF-1	0–1	6.81	5.85	2.99
	1–2	8.60	1.75	1.74
	2–3	8.95	6.4	3.17
	3–4	7.96	1.52	0.92
	4–5	14.32	1.51	1.11
NF-2	0–1	1.36	1.35	1.16
	1–2	2.27	0.00	2.49
	2–3	1.31	1.56	1.25
	3–4	3.63	9.21	3.44
	4–5	2.35	5.15	1.36
NF-3	0–1	2.14	2.69	4.81
	1–2	4.08	2.32	2.34
	2–3	5.16	4.27	2.35
	3–4	4.36	6.08	5.07
	4–5	4.75	3.44	1.76
NF-4	0–1	0.87	0.00	0.00
	1–2	13.07	0.82	0.82
	2–3	5.50	3.09	1.70
	3–4	0.66	1.74	1.29
	4–5	1.24	1.27	1.29
NF-5	0–1	2.11	7.34	2.74
	1–2	2.10	12.00	4.05
	2–3	3.81	3.82	1.61
	3–4	7.41	5.33	2.11
	4–5	4.76	2.11	0.60
SF-1	0–1	3.76	7.79	5.81
	1–2	4.21	7.35	7.71
	2–3	2.17	5.12	3.53
	3–4	6.52	1.81	1.76
	4–5	3.59	6.75	5.34

Station	Core depth (cm)	Chlorophyll Degradation Products		
		% Pheo *a*	% Pheoph *a*	% Pyropheoph *a*
SF-2	0–1	0.78	12.10	8.04
	1–2	1.25	5.02	6.14
	2–3	16.48	1.18	0.81
	3–4	3.83	5.22	1.93
	4–5	9.65	2.56	1.00
SF-3	0–1	0.42	5.63	4.43
	1–2	0.00	9.70	1.87
	2–3	4.93	5.10	2.82
	3–4	6.09	3.15	2.46
	4–5	2.80	9.01	5.53
SF-4	1–2	5.85	17.47	2.52
	2–3	6.84	13.88	1.44
	3–4	0.20	18.68	2.11
	4–5	3.89	2.64	1.77
SF-5	0–1	1.25	6.25	2.60
	1–2	0.64	13.23	4.69
	2–3	0.47	12.19	5.18
	3–4	0.65	4.17	1.86
	4–5	0.64	9.75	2.78
SF-6	0–1	4.31	7.08	0.00
	1–2	10.20	16.29	1.10
	2–3	18.43	5.10	1.49
	3–4	4.07	1.91	1.30
	4–5	2.49	3.66	1.95

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Table 2c. Carotenoids.

Station	Core depth (cm)	Carotenoids					
		% Peridin	% Fucox	% Diatox	% Lutein	% Zeax	% Canthax
NF-1	0–1	0.00	0.00	0.00	0.00	0.00	5.91
	1–2	1.87	2.76	0.00	0.00	0.00	0.00
	2–3	3.43	5.21	0.00	0.00	0.00	0.00
	3–4	2.55	2.68	0.00	0.00	0.00	0.00
	4–5	1.65	0.00	0.00	0.00	0.00	3.92
NF-2	0–1	2.20	0.95	8.33	4.43	6.98	1.71
	1–2	4.84	4.23	0.00	4.91	0.00	2.55
	2–3	2.97	2.06	12.66	3.66	3.38	4.53
	3–4	0.00	0.00	9.12	3.03	2.98	3.89
	4–5	0.00	0.00	0.00	3.48	3.26	3.10
NF-3	0–1	3.24	2.64	9.62	0.97	0.00	6.11
	1–2	2.94	2.76	11.73	0.00	0.00	5.25
	2–3	2.79	2.76	5.28	4.08	0.88	2.71
	3–4	0.00	0.00	0.00	2.79	0.00	4.72
	4–5	2.55	2.62	4.64	1.43	2.84	7.42
NF-4	0–1	2.97	2.57	6.98	9.41	0.00	3.85
	1–2	2.40	1.70	6.25	3.08	3.30	4.62
	2–3	2.60	1.94	4.60	3.08	2.97	4.88
	3–4	2.06	2.11	7.73	0.00	0.00	7.32
	4–5	2.44	2.17	7.09	2.13	0.00	7.11
NF-5	0–1	0.00	0.00	8.59	2.32	3.02	2.22
	1–2	0.00	0.00	8.32	2.76	1.01	3.10
	2–3	5.11	4.79	9.20	2.99	0.90	2.24
	3–4	2.03	2.99	6.75	2.73	0.00	4.08
	4–5	2.30	0.00	3.23	1.97	0.00	4.32
SF-1	0–1	0.00	0.00	0.00	4.7	0.00	2.80
	1–2	0.00	0.00	0.00	0.00	0.00	0.00
	2–3	2.73	2.32	0.00	0.00	0.00	5.21
	3–4	0.00	0.00	0.00	0.00	0.00	0.00
	4–5	0.00	0.00	0.00	3.45	0.00	5.61
SF-2	0–1	0.00	0.00	6.14	1.54	3.02	1.63
	1–2	4.49	0.00	7.70	1.90	4.10	3.29
	2–3	0.00	0.00	0.00	0.00	0.00	5.35
	3–4	0.00	0.00	0.00	8.83	1.72	7.55
	4–5	0.00	0.00	0.00	0.00	0.00	5.04
SF-3	0–1	1.21	1.91	0.88	0.52	1.30	1.90
	1–2	0.88	1.17	1.52	3.22	1.15	1.85
	2–3	2.42	2.37	2.80	1.25	0.59	2.78
	3–4	3.61	3.25	0.00	0.00	0.00	0.00
	4–5	4.19	4.21	0.00	4.15	0.00	3.91
SF-4	1–2	0.61	2.14	1.30	0.00	0.00	1.41
	2–3	0.71	1.93	2.18	0.00	0.00	2.27
	3–4	1.10	2.14	0.00	0.00	0.70	1.09
	4–5	5.55	6.57	0.00	0.00	0.00	5.09
SF-5	0–1	0.00	0.00	1.99	0.00	0.00	3.63
	1–2	0.00	0.00	3.32	0.00	0.00	2.04
	2–3	0.00	0.00	3.32	1.01	1.81	1.16
	3–4	2.38	1.50	2.28	4.31	0.00	3.18
	4–5	0.00	0.00	3.02	0.00	2.88	2.67
SF-6	0–1	0.00	9.30	5.46	0.00	0.00	3.19
	1–2	0.95	1.62	0.00	0.00	0.00	1.92
	2–3	2.25	0.74	4.69	0.90	0.00	2.82
	3–4	2.41	3.52	0.00	0.00	0.00	0.00
	4–5	3.27	3.47	7.68	0.00	0.00	8.61

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Table 3. Fatty acid concentrations expressed in mgkg^{-1} DW. The only station sampled with the box-corer, NF-5, is marked in dark grey. No sediment was available for the following samples: NF-4 2–3 cm, SF-2 2–3 cm.

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Table 3a. PUFA.

Station	Core depth (cm)	PUFA (mg kg^{-1}) 22 : 2	22 : 6
NF-1	0–1	0.109	0.109
	1–2	0.000	0.000
	2–3	0.000	0.000
	3–4	0.009	0.000
	4–5	0.101	0.101
NF-2	0–1	0.119	0.000
	1–2	0.047	0.000
	2–3	0.000	0.000
	3–4	0.018	0.000
	4–5	0.009	0.000
NF-3	0–1	0.109	0.109
	1–2	0.105	0.105
	2–3	0.009	0.000
	3–4	0.102	0.102
	4–5	0.000	0.000
NF-4	0–1	0.103	0.103
	1–2	0.099	0.099
	3–4	0.000	0.000
	4–5	0.108	0.108
NF-5	0–1	0.052	0.000
	1–2	0.000	0.000
	2–3	0.043	0.000
	3–4	0.000	0.000
	4–5	0.009	0.000
SF-1	0–1	0.104	0.030
	1–2	0.099	0.099
	2–3	0.101	0.101
	3–4	0.095	0.095
	4–5	0.109	0.109
SF-2	0–1	0.090	0.297
	1–2	0.024	0.000
	3–4	0.009	0.000
	4–5	0.009	0.000
SF-3	0–1	0.109	0.109
	1–2	0.009	0.000
	2–3	0.000	0.141
	3–4	0.000	0.000
	4–5	0.105	0.105
SF-4	0–1	0.000	0.000
	1–2	0.000	0.142
	2–3	0.000	0.000
	3–4	0.009	0.000
	4–5	0.100	0.100
SF-5	0–1	0.105	0.000
	1–2	0.097	0.000
	2–3	0.011	0.000
	3–4	0.082	0.000
	4–5	0.009	0.000
SF-6	0–1	0.104	0.104
	1–2	0.000	0.000
	2–3	0.000	0.000
	3–4	0.000	0.000
	4–5	0.111	0.111

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Table 3b. MUFA.

Station	Core depth (cm)	MUFA (mg kg^{-1})						
		16 : 1	18 : 1trans	18 : 1	18 : 1cis	20 : 1	22 : 1	24 : 1
NF-1	0–1	0.088	0.017	0.032	0.013	0.109	0.109	0.109
	1–2	0.160	0.000	0.379	0.456	0.253	2.707	0.099
	2–3	0.127	0.000	0.314	0.364	0.000	0.000	0.000
	3–4	0.172	0.121	0.255	0.285	0.000	0.000	0.000
	4–5	0.236	0.023	0.050	0.088	0.101	0.101	0.101
NF-2	0–1	0.175	0.384	0.378	4.522	0.450	8.452	0.202
	1–2	0.447	0.284	0.400	2.257	0.339	5.604	0.192
	2–3	0.138	0.178	0.346	1.466	0.241	3.302	0.132
	3–4	0.221	0.149	0.309	0.729	0.169	1.509	0.127
	4–5	0.224	0.160	0.297	0.749	0.165	1.457	0.122
NF-3	0–1	0.407	0.049	0.086	0.289	0.109	0.109	0.109
	1–2	0.325	0.036	0.068	0.195	0.105	0.105	0.105
	2–3	0.188	0.117	0.256	0.269	0.155	0.154	0.000
	3–4	0.026	0.102	0.203	0.007	0.102	0.102	0.102
	4–5	0.000	0.000	0.010	0.222	0.000	0.000	0.000
NF-4	0–1	0.342	0.039	0.064	0.173	0.103	0.103	0.103
	1–2	0.220	0.033	0.047	0.185	0.099	0.099	0.099
	3–4	0.100	0.000	0.243	0.294	0.000	0.000	0.000
	4–5	0.355	0.069	0.068	0.366	0.108	0.108	0.108
NF-5	0–1	0.351	0.297	0.411	3.233	0.371	4.861	0.201
	1–2	0.117	0.126	0.273	0.951	0.169	1.135	0.096
	2–3	0.323	0.417	0.356	2.284	0.279	4.019	0.170
	3–4	0.096	0.095	0.230	0.427	0.146	0.405	0.000
	4–5	0.156	0.223	0.253	0.624	0.155	0.990	0.115
SF-1	0–1	0.630	0.111	0.125	0.912	0.104	0.104	0.104
	1–2	0.500	0.108	0.095	0.900	0.099	0.099	0.099
	2–3	0.209	0.052	0.057	0.260	0.101	0.101	0.101
	3–4	0.190	0.059	0.070	0.246	0.095	0.095	0.095
	4–5	0.140	0.046	0.054	0.365	0.109	0.109	0.109
SF-2	0–1	0.722	0.300	0.672	4.434	0.452	7.192	0.249
	1–2	0.270	0.171	0.335	1.058	0.188	1.777	0.135
	3–4	0.151	0.213	0.250	0.563	0.153	0.951	0.000
	4–5	0.161	0.256	0.261	1.053	0.206	2.529	0.142
SF-3	0–1	1.125	0.286	0.481	2.006	0.109	0.109	0.109
	1–2	0.382	0.226	0.391	1.800	0.000	0.135	0.000
	2–3	0.150	0.141	0.372	0.541	0.000	0.105	0.000
	3–4	0.145	0.126	0.358	0.712	0.000	0.091	0.000
	4–5	0.738	0.111	0.150	1.221	0.105	0.105	0.105
SF-4	0–1	0.200	0.180	0.508	1.454	0.154	0.113	0.000
	1–2	0.199	0.194	0.480	1.190	0.000	0.000	0.000
	2–3	0.119	0.140	0.294	0.479	0.000	0.000	0.000
	3–4	0.451	0.285	0.432	1.282	0.182	0.153	0.000
	4–5	0.499	0.065	0.106	0.565	0.100	0.100	0.100
SF-5	0–1	0.755	0.551	0.704	5.785	0.572	8.648	0.000
	1–2	0.195	0.184	0.497	2.452	0.000	0.000	0.160
	2–3	0.302	0.181	0.377	1.212	0.201	1.745	0.143
	3–4	0.175	0.178	0.429	2.376	0.254	3.375	0.134
	4–5	0.389	0.203	0.431	1.724	0.199	1.864	0.130
SF-6	0–1	0.224	0.072	0.114	0.457	0.104	0.104	0.104
	1–2	0.121	0.099	0.304	0.538	0.000	0.000	0.000
	2–3	0.142	0.155	0.345	1.061	0.000	0.000	0.000
	3–4	0.112	0.109	0.293	0.421	0.193	0.000	0.000
	4–5	0.391	0.083	0.138	0.632	0.111	0.111	0.111

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Table 3c. MC-FA.

Station	Core depth (cm)	MC-FA (mg kg^{-1})													
		12 : 0	iso14 : 0	14 : 0	iso15 : 0	anteiso15 : 0	15 : 0	iso16 : 0	16 : 0	iso17 : 0	anteiso17 : 0	17 : 0	18 : 0	19 : 0	20 : 0
NF-1	0–1	0.218	0.041	0.153	0.071	0.157	0.041	0.033	0.577	0.052	0.026	0.015	0.175	0.432	0.040
	1–2	0.213	0.209	0.777	0.312	0.421	0.228	0.345	1.919	0.217	0.211	0.155	0.630	24.527	0.313
	2–3	0.000	0.169	0.442	0.207	0.290	0.153	0.291	1.209	0.175	0.143	0.137	0.468	15.108	0.234
	3–4	0.000	0.228	0.242	0.156	0.203	0.133	0.373	0.674	0.146	0.135	0.121	0.241	0.645	0.256
	4–5	0.164	0.076	0.545	0.210	0.346	0.143	0.107	1.437	0.174	0.148	0.071	0.372	1.903	0.139
NF-2	0–1	0.437	0.000	0.613	0.265	0.323	0.240	0.302	2.054	0.201	0.204	0.146	1.250	2.667	0.344
	1–2	0.315	0.000	0.666	0.358	0.462	0.268	0.457	2.179	0.274	0.230	0.197	1.120	2.779	0.475
	2–3	0.197	0.183	0.543	0.126	0.267	0.348	0.335	1.Chl *a*	0.201	0.164	0.136	0.828	2.445	0.265
	3–4	0.000	0.000	0.255	0.187	0.207	0.161	0.396	1.021	0.182	0.154	0.143	0.606	1.850	0.338
	4–5	0.000	0.237	0.346	0.223	0.263	0.178	0.392	1.099	0.176	0.171	0.144	0.517	1.644	0.319
NF-3	0–1	0.201	0.098	0.751	0.317	0.468	0.231	0.150	3.476	0.399	0.169	0.121	0.794	1.867	0.252
	1–2	0.208	0.101	0.660	0.279	0.370	0.200	0.116	1.713	0.197	0.135	0.094	0.555	1.505	0.165
	2–3	0.000	0.000	0.219	0.153	0.231	0.124	0.356	0.638	0.156	0.135	0.117	0.228	0.523	0.236
	3–4	0.203	0.026	0.041	0.024	0.032	0.021	0.013	0.282	0.011	0.008	0.007	0.000	0.029	0.203
	4–5	0.000	0.000	0.153	0.000	0.000	0.000	0.000	0.327	0.000	0.000	0.000	0.173	0.199	0.136
NF-4	0–1	0.196	0.094	0.609	0.260	0.323	0.164	0.105	2.349	0.193	0.154	0.091	0.634	2.621	0.216
	1–2	0.156	0.072	0.473	0.207	0.323	0.138	0.092	1.689	0.125	0.120	0.075	0.514	2.010	0.162
	3–4	0.000	0.000	0.221	0.107	0.135	0.105	0.251	0.590	0.095	0.098	0.081	0.252	0.873	0.164
	4–5	0.183	0.076	0.516	0.263	0.332	0.139	0.104	1.601	0.195	0.101	0.071	0.536	2.160	0.118
NF-5	0–1	0.000	0.291	0.457	0.264	0.314	0.264	0.493	1.861	0.237	0.228	0.196	1.175	2.903	0.411
	1–2	0.187	0.159	0.328	0.150	0.214	0.141	0.262	0.859	0.119	0.099	0.096	0.448	1.068	0.198
	2–3	0.280	0.258	0.541	0.268	0.313	0.254	0.429	2.078	0.221	0.210	0.183	1.198	2.933	0.378
	3–4	0.000	0.000	0.204	0.102	0.154	0.087	0.243	0.462	0.095	0.083	0.079	0.270	0.697	0.159
	4–5	0.000	0.000	0.219	0.144	0.174	0.147	0.376	0.867	0.147	0.136	0.131	0.583	1.270	0.275
SF-1	0–1	0.233	0.094	0.649	0.256	0.319	0.160	0.102	1.963	0.201	0.101	0.097	0.433	1.949	0.165
	1–2	0.239	0.096	0.685	0.250	0.322	0.150	0.107	1.587	0.149	0.114	0.077	0.443	1.993	0.148
	2–3	0.145	0.059	0.487	0.154	0.272	0.118	0.092	1.402	0.145	0.096	0.054	0.350	1.755	0.149
	3–4	0.116	0.055	0.401	0.131	0.226	0.104	0.063	0.252	0.128	0.118	0.066	0.444	1.829	0.107
	4–5	0.217	0.049	0.384	0.106	0.211	0.108	0.073	0.981	0.117	0.080	0.045	0.299	2.042	0.092
SF-2	0–1	0.406	0.326	0.839	0.471	0.476	0.333	0.563	3.001	0.384	0.296	0.245	1.413	2.511	0.498
	1–2	0.000	0.000	0.286	0.187	0.213	0.173	0.401	1.046	0.192	0.161	0.143	0.496	1.412	0.323
	3–4	0.000	0.000	0.228	0.141	0.165	0.149	0.374	0.905	0.144	0.136	0.131	0.512	1.261	0.288
	4–5	0.000	0.000	0.364	0.174	0.215	0.193	0.399	1.136	0.142	0.202	0.151	0.766	2.466	0.369
SF-3	0–1	0.458	0.335	1.680	0.756	0.821	0.488	0.287	5.941	0.607	0.286	0.281	2.730	3.528	0.543
	1–2	0.000	0.241	0.520	0.269	0.304	0.206	0.401	1.508	0.209	0.253	0.157	0.438	8.500	0.287
	2–3	0.000	0.000	0.463	0.250	0.272	0.172	0.295	1.607	0.196	0.144	0.135	0.693	1.267	0.242
	3–4	0.000	0.163	0.428	0.213	0.247	0.158	0.286	1.231	0.172	0.177	0.112	0.435	1.022	0.214
	4–5	0.296	0.121	0.888	0.411	0.523	0.253	0.165	2.232	0.326	0.148	0.103	0.628	1.912	0.238
SF-4	0–1	0.242	0.212	0.841	0.397	0.460	0.266	0.348	2.442	0.285	0.283	0.198	0.788	19.831	0.325
	1–2	0.000	0.213	0.886	0.000	0.493	0.289	0.396	2.784	0.294	0.323	0.191	0.778	2.140	0.328
	2–3	0.000	0.000	0.294	0.143	0.197	0.129	0.268	1.011	0.127	0.141	0.108	0.616	0.581	0.180
	3–4	0.000	0.268	0.685	0.324	0.420	0.245	0.443	2.210	0.253	0.253	0.194	0.991	13.459	0.343
	4–5	0.194	0.111	0.723	0.348	0.521	0.222	0.154	1.975	0.302	0.138	0.118	0.683	1.855	0.264
SF-5	0–1	0.600	0.438	1.358	0.774	0.799	0.504	0.748	5.610	0.495	0.176	0.329	2.683	5.495	0.796
	1–2	0.269	0.229	0.718	0.391	0.437	0.262	0.389	2.268	0.275	0.198	0.174	1.024	2.017	0.344
	2–3	0.000	0.000	0.387	0.250	0.288	0.206	0.451	1.226	0.215	0.176	0.161	0.550	1.159	0.342
	3–4	0.352	0.203	0.755	0.365	0.405	0.256	0.294	2.282	0.247	0.182	0.157	1.015	1.889	0.302
	4–5	0.323	0.263	0.584	0.344	0.394	0.254	0.442	1.915	0.246	0.197	0.178	0.769	1.657	0.381
SF-6	0–1	0.207	0.055	0.438	0.188	0.272	0.104	0.081	1.237	0.110	0.068	0.057	0.385	0.874	0.046
	1–2	0.000	0.162	0.342	0.173	0.206	0.134	0.269	0.925	0.136	0.151	0.098	0.341	6.895	0.196
	2–3	0.000	0.163	0.404	0.197	0.289	0.163	0.286	1.216	0.174	0.254	0.118	0.441	1.031	0.199
	3–4	0.000	0.151	0.254	0.140	0.186	0.121	0.265	0.842	0.130	0.160	0.097	0.352	0.874	0.193
	4–5	0.197	0.098	0.715	0.300	0.404	0.178	0.146	2.061	0.225	0.136	0.104	1.134	2.127	0.152

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Table 3d. LC-FA.

Station	Core depth (cm)	LC-FA (mg kg^{-1})									
		21 : 0	22 : 0	23 : 0	24 : 0	25 : 0	26 : 0	27 : 0	28 : 0	29 : 0	30 : 0
NF-1	0–1	0.001	0.054	0.109	0.030	0.109	0.005	0.109	0.015	0.109	0.109
	1–2	0.138	0.315	0.099	0.346	0.117	0.257	0.097	0.171	0.094	0.164
	2–3	0.145	0.000	0.077	0.255	0.098	0.205	0.091	0.149	0.085	0.126
	3–4	0.011	0.311	0.090	0.149	0.145	0.221	0.143	0.178	0.000	0.197
	4–5	0.015	0.169	0.019	0.202	0.046	0.131	0.101	0.043	0.101	0.224
NF-2	0–1	1.855	0.362	0.095	0.331	0.140	0.264	0.097	0.175	0.100	0.166
	1–2	0.837	0.519	0.127	0.307	0.191	0.363	0.163	0.230	0.000	0.000
	2–3	0.010	0.298	0.089	0.263	0.111	0.187	0.000	0.120	0.000	0.000
	3–4	0.472	0.419	0.111	0.439	0.193	0.390	0.165	0.278	0.158	0.266
	4–5	0.512	0.385	0.106	0.241	0.186	0.336	0.160	0.247	0.153	0.301
NF-3	0–1	0.024	0.518	0.056	0.285	0.109	0.158	0.109	0.047	0.109	0.231
	1–2	0.012	0.279	0.105	0.182	0.025	0.085	0.105	0.022	0.105	0.105
	2–3	0.010	0.275	0.078	0.131	0.131	0.195	0.131	0.163	0.000	0.000
	3–4	0.010	0.203	0.102	0.102	0.102	0.102	0.102	0.102	0.102	0.102
	4–5	0.010	0.111	0.000	0.086	0.000	0.000	0.000	0.000	0.000	0.000
NF-4	0–1	0.022	0.373	0.103	0.213	0.028	0.102	0.103	0.027	0.103	0.219
	1–2	0.014	0.314	0.025	0.191	0.049	0.128	0.015	0.055	0.099	0.218
	3–4	0.011	0.147	0.062	0.134	0.089	0.124	0.000	0.106	0.000	0.000
	4–5	0.015	0.222	0.016	0.186	0.024	0.132	0.108	0.054	0.108	0.245
NF-5	0–1	0.746	0.513	0.130	0.295	0.258	0.425	0.198	0.309	0.191	0.315
	1–2	0.010	0.194	0.068	0.192	0.093	0.160	0.089	0.119	0.000	0.097
	2–3	0.710	0.451	0.122	0.274	0.198	0.354	0.163	0.245	0.159	0.212
	3–4	0.134	0.143	0.058	0.129	0.086	0.117	0.000	0.099	0.000	0.000
	4–5	0.293	0.333	0.093	0.174	0.166	0.268	0.153	0.205	0.148	0.000
SF-1	0–1	0.013	0.273	0.026	0.185	0.037	0.072	0.104	0.072	0.104	0.216
	1–2	0.015	0.000	0.041	0.152	0.002	0.066	0.099	0.017	0.099	0.099
	2–3	0.009	0.097	0.020	0.094	0.023	0.035	0.101	0.023	0.101	0.205
	3–4	0.018	0.232	0.028	0.262	0.030	0.155	0.095	0.052	0.095	0.216
	4–5	0.011	0.192	0.016	0.148	0.020	0.093	0.109	0.027	0.109	0.237
SF-2	0–1	1.115	0.621	0.149	0.404	0.320	0.487	0.209	0.335	0.000	0.319
	1–2	0.416	0.402	0.107	0.247	0.179	0.339	0.167	0.257	0.160	0.251
	3–4	0.266	0.356	0.100	0.201	0.167	0.291	0.153	0.225	0.000	0.179
	4–5	0.806	0.448	0.120	0.246	0.205	0.336	0.138	0.247	0.000	0.291
SF-3	0–1	0.048	0.783	0.162	0.756	0.170	0.517	0.109	0.283	0.109	0.288
	1–2	0.010	0.367	0.099	0.225	0.164	0.309	0.151	0.222	0.000	0.271
	2–3	0.146	0.243	0.081	0.269	0.100	0.214	0.089	0.145	0.089	0.125
	3–4	0.010	0.214	0.072	0.219	0.092	0.174	0.121	0.092	0.084	0.121
	4–5	0.018	0.402	0.028	0.287	0.103	0.153	0.105	0.074	0.105	0.250
SF-4	0–1	1.148	0.374	0.114	0.438	0.122	0.331	0.000	0.196	0.098	0.165
	1–2	0.011	0.339	0.104	0.376	0.114	0.280	0.102	0.176	0.097	0.156
	2–3	0.011	0.168	0.067	0.161	0.094	0.138	0.000	0.109	0.000	0.000
	3–4	0.850	0.431	0.119	0.323	0.184	0.421	0.176	0.287	0.160	0.000
	4–5	0.025	0.489	0.073	0.404	0.105	0.267	0.100	0.111	0.100	0.231
SF-5	0–1	1.530	0.936	0.225	0.616	0.000	0.717	0.320	0.469	0.000	0.374
	1–2	0.200	0.369	0.104	0.367	0.150	0.273	0.124	0.174	0.000	0.153
	2–3	0.480	0.434	0.113	0.241	0.195	0.319	0.175	0.232	0.214	0.200
	3–4	0.138	0.334	0.085	0.281	0.121	0.201	0.000	0.125	0.000	0.000
	4–5	0.011	0.461	0.118	0.338	0.187	0.414	0.168	0.264	0.153	0.235
SF-6	0–1	0.005	0.072	0.021	0.079	0.020	0.032	0.104	0.104	0.104	0.104
	1–2	0.440	0.186	0.072	0.203	0.092	0.166	0.000	0.115	0.000	0.090
	2–3	0.011	0.212	0.073	0.214	0.097	0.171	0.000	0.123	0.000	0.133
	3–4	0.135	0.189	0.071	0.189	0.092	0.158	0.000	0.118	0.000	0.096
	4–5	0.018	0.257	0.040	0.238	0.025	0.138	0.111	0.049	0.111	0.242

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Table 4. Caption on next page.

Station	Core depth (cm)	THAA (nmol mg^{-1})																
		Asp	Ser	Glu	Gly	His	Arg	Thr	Ala	Pro	Tyr	Val	Lys	Ile	Leu	Phe	Bala	Gaba
NF-1	0–1	0.966	1.646	0.903	3.756	0.272	1.054	1.540	1.087	0.845	0.350	0.767	0.338	0.380	0.655	0.534	0.000	0.095
	1–2	1.139	1.538	0.954	4.109	0.248	1.043	1.568	1.201	0.954	0.337	0.871	0.446	0.452	0.766	0.535	0.038	0.111
	2–3	0.888	2.283	0.939	5.306	0.376	1.617	2.562	1.309	1.133	0.632	1.099	0.302	0.512	0.917	1.008	0.044	0.254
	3–4	0.901	1.733	0.828	4.152	0.240	1.265	1.896	1.192	0.952	0.429	0.901	0.317	0.433	0.742	0.695	0.040	0.176
	4–5	0.678	1.128	0.639	2.348	0.229	0.792	0.954	1.017	0.666	0.172	0.597	0.445	0.300	0.517	0.311	0.026	0.000
NF-2	0–1	0.974	1.519	0.902	4.432	0.429	1.083	1.527	1.122	0.787	0.281	0.769	0.332	0.354	0.621	0.451	0.034	0.128
	1–2	0.836	1.263	0.742	3.195	0.503	0.718	1.103	0.875	0.669	0.212	0.548	0.291	0.239	0.518	0.403	0.034	0.088
	2–3	0.546	0.834	0.444	2.238	0.177	0.667	0.950	0.839	0.592	0.184	0.576	0.338	0.279	0.481	0.349	0.032	0.163
	3–4	0.534	1.477	0.667	3.212	0.343	1.277	1.664	0.836	0.712	0.436	0.738	0.187	0.347	0.578	0.756	0.036	0.000
	4–5	0.491	2.085	0.700	4.081	0.626	1.415	1.460	0.834	0.819	0.760	0.849	0.187	0.343	0.655	1.445	0.000	0.339
NF-3	0–1	1.064	1.149	0.801	2.616	0.076	0.706	0.905	1.326	0.741	0.189	0.625	0.615	0.312	0.557	0.280	0.084	0.230
	1–2	1.076	1.481	1.056	3.059	0.353	1.065	1.234	1.292	0.876	0.238	0.766	0.546	0.411	0.701	0.436	0.033	0.000
	2–3	1.478	1.114	1.045	2.842	0.563	0.661	0.965	1.259	0.798	0.172	0.698	0.576	0.354	0.616	0.354	0.056	0.098
	3–4	0.888	1.967	1.030	3.900	0.421	1.200	1.735	1.160	0.984	0.411	0.971	0.399	0.464	0.826	0.699	0.044	0.053
	4–5	1.868	1.371	1.368	3.803	0.282	0.983	1.234	1.692	0.961	0.246	0.810	0.767	0.412	0.725	0.370	0.048	0.101
NF-4	0–1	1.155	0.734	0.744	1.959	0.340	0.589	0.705	1.003	0.537	0.128	0.485	0.426	0.249	0.416	0.261	0.051	0.071
	1–2	0.748	1.044	0.651	2.271	0.254	0.839	0.996	0.804	0.586	0.192	0.573	0.309	0.286	0.472	0.397	0.042	0.035
	2–3	0.572	0.814	0.516	2.584	0.442	0.632	0.943	0.651	0.453	0.184	0.453	0.171	0.208	0.366	0.295	0.022	0.110
	3–4	0.900	0.661	0.607	1.633	0.442	0.604	0.658	0.745	0.495	0.121	0.466	0.357	0.230	0.377	0.221	0.046	0.031
	4–5	0.904	0.916	0.765	2.651	0.596	0.671	0.871	0.810	0.568	0.162	0.544	0.334	0.266	0.450	0.287	0.044	0.107
NF-5	0–1	0.720	1.183	0.623	2.666	0.257	1.036	1.272	0.779	0.598	0.295	0.594	0.232	0.270	0.459	0.573	0.032	0.000
	1–2	0.643	1.594	0.757	4.003	0.391	1.085	1.379	0.942	0.765	0.311	0.694	0.261	0.320	0.547	0.585	0.056	0.209
	2–3	0.974	1.020	0.732	3.162	0.721	0.758	1.043	0.942	0.672	0.173	0.620	0.369	0.288	0.516	0.334	0.043	0.142
	3–4	1.004	0.850	0.772	2.679	0.428	0.656	0.918	0.905	0.601	0.156	0.571	0.377	0.277	0.463	0.302	0.038	0.113
	4–5	0.361	1.345	0.541	3.182	0.139	1.107	1.362	0.607	0.566	0.353	0.599	0.377	0.277	0.451	0.722	0.034	0.776
SF-1	0–1	0.897	1.160	0.795	2.439	0.284	0.835	1.088	0.919	0.685	0.227	0.637	0.384	0.344	0.570	0.422	0.036	0.024
	1–2	0.797	1.513	0.705	3.220	0.307	1.063	1.528	0.787	0.716	0.363	0.716	0.245	0.322	0.572	0.710	0.019	0.000
	2–3	0.803	1.378	0.724	3.617	0.505	0.909	1.506	0.926	0.738	0.294	0.716	0.281	0.320	0.566	0.531	0.045	0.136
	3–4	0.931	1.192	0.743	3.495	0.383	0.749	1.096	0.848	0.657	0.201	0.624	0.337	0.290	0.485	0.350	0.045	0.066
	4–5	0.656	1.569	0.577	3.200	0.406	1.155	1.623	0.741	0.726	0.414	0.695	0.234	0.258	0.538	0.851	0.000	0.000
SF-2	0–1	1.334	3.474	1.437	6.548	0.853	2.135	3.228	1.683	1.545	0.870	1.511	0.441	0.710	1.294	1.580	0.064	0.118
	1–2	1.055	1.776	0.962	4.319	0.405	1.149	1.719	1.153	0.931	0.338	0.886	0.378	0.427	0.726	0.637	0.043	0.125
	3–4	0.427	1.544	0.602	3.623	0.197	0.876	1.215	0.602	0.613	0.449	0.657	0.378	0.241	0.515	0.920	0.000	0.998
SF-3	1–2	1.552	1.588	1.286	3.844	0.428	0.956	1.398	1.462	1.034	0.235	0.903	0.632	0.472	0.783	0.489	0.058	0.058
	2–3	2.560	3.570	0.926	6.029	0.909	2.374	3.671	1.162	1.330	1.061	1.313	0.632	0.488	0.909	2.290	0.000	0.372
	3–4	1.437	1.962	1.222	4.428	0.532	1.177	1.735	1.597	1.212	0.324	1.065	0.680	0.561	0.917	0.632	0.051	0.034
	4–5	1.334	1.751	1.110	3.718	0.740	1.056	1.622	1.418	1.070	0.291	1.012	0.546	0.462	0.787	0.510	0.048	0.111
SF-4	0–1	1.141	2.312	1.147	5.011	0.397	1.521	2.256	1.588	1.170	0.447	1.030	0.464	0.528	0.931	0.776	0.096	0.737
	1–2	1.238	2.507	1.244	5.436	0.431	1.649	2.447	1.722	1.269	0.484	1.118	0.503	0.573	1.010	0.842	0.057	0.152
	2–3	2.198	1.741	1.521	3.499	0.312	1.344	1.503	1.865	1.166	0.294	0.950	0.901	0.532	0.908	0.464	0.000	0.000
	3–4	1.018	1.671	0.809	3.793	0.264	1.201	1.821	1.585	1.160	0.342	0.990	0.678	0.531	0.929	0.584	0.000	0.000
	4–5	1.539	1.216	1.125	3.352	0.397	0.807	1.050	1.412	0.835	0.200	0.748	0.619	0.350	0.619	0.320	0.033	0.072
SF-5	0–1	1.263	1.957	1.164	4.001	0.351	1.155	1.626	1.410	1.117	0.272	0.997	0.614	0.518	0.872	0.629	0.064	0.000
	1–2	1.249	1.650	1.057	4.078	0.368	0.995	1.471	1.359	1.015	0.231	0.938	0.552	0.443	0.751	0.438	0.066	0.098
	2–3	1.021	2.506	1.215	5.810	0.409	1.589	2.450	1.354	1.128	0.477	1.049	0.334	0.516	0.886	0.949	0.053	0.273
	3–4	0.979	2.446	1.140	5.227	0.572	1.513	2.319	1.306	1.106	0.496	1.043	0.369	0.504	0.890	0.950	0.045	0.201
	4–5	0.982	2.386	1.176	4.598	0.446	1.478	2.130	1.432	1.121	0.442	1.048	0.450	0.551	0.920	0.908	0.049	0.040
SF-6	0–1	0.943	2.141	1.010	4.476	0.428	1.409	2.016	1.358	1.070	0.399	0.965	0.380	0.502	0.853	0.751	0.054	0.117
	1–2	1.085	2.024	1.082	4.471	0.347	1.356	1.921	1.438	1.074	0.359	0.938	0.421	0.482	0.844	0.662	0.049	0.113
	2–3	1.167	2.900	1.387	5.729	0.584	1.913	2.694	1.702	1.383	0.597	1.257	0.480	0.651	1.127	1.118	0.068	0.079
	3–4	0.565	2.562	0.666	5.519	0.571	1.873	2.875	1.461	1.261	0.713	1.190	0.295	0.548	0.966	1.261	0.053	0.487

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Table 4. Amino acid concentrations expressed in nmol mg^{-1} DW. (Abbreviations: Asp, aspartic acid; Ser, serine; Glu, glutamic acid; Gly, glycine; His, histidine; Arg, arginine; Thr, threonine; Ala, alanine; Pro, proline; Tyr, tyrosine; Val, valine; Lys, lysine; Ile, isoleucine; Leu, leucine; Phe, phenylalanine; BALA, β-alanine; GABA, γ-aminobutyric acid). The only station sampled with the box-corer, NF-5, is marked in dark grey. No sediment was available for the following samples: SF-2 from 2 to 3 cm, SF-2 from 4 to 5 cm, SF-3 from 0 to 1 cm, SF-6 from 4 to 5 cm.

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Table 5. Carbohydrates concentrations expressed in mg g^{-1} DW. No sediment was available for the following samples: NF-1 from 2 to 3 cm, SF-4 from 0 to 1 cm, SF-6 from 0 to 1 cm.

Station	Core depth (cm)	Glucose (mg g^{-1})	Xylose (mg g^{-1})	Rhamnose (mg g^{-1})	Mannose (mg g^{-1})
NF-1	0–1	0.076	0.089	0.273	0.050
	1–2	0.112	0.113	0.233	0.066
	3–4	0.050	0.040	0.116	0.069
	4–5	0.084	0.067	0.252	0.027
NF-3	0–1	0.077	0.099	0.255	0.041
	1–2	0.093	0.049	0.230	0.025
	2–3	0.099	0.087	0.298	0.153
	3–4	0.176	0.063	0.278	0.082
	4–5	0.078	0.092	0.284	0.027
NF-4	0–1	0.066	0.048	0.156	0.010
	1–2	0.071	0.047	0.247	0.051
	2–3	0.056	0.038	0.196	0.052
	3–4	0.071	0.063	0.171	0.017
	4–5	0.051	0.046	0.164	0.015
SF-1	0–1	0.056	0.059	0.172	0.017
	1–2	0.233	0.083	0.383	0.117
	2–3	0.196	0.080	0.321	0.091
	3–4	0.113	0.054	0.246	0.063
	4–5	0.085	0.028	0.173	0.074
SF-3	0–1	0.084	0.212	0.020	0.036
	1–2	0.065	0.086	0.344	0.020
	2–3	0.199	0.307	0.516	0.100
	3–4	0.081	0.038	0.194	0.049
	4–5	0.062	0.080	0.224	0.058
SF-4	1–2	0.060	0.052	0.242	0.037
	2–3	0.051	0.043	0.149	0.016
	3–4	0.048	0.122	0.425	0.090
	4–5	0.100	0.127	0.417	0.050
SF-6	1–2	0.073	0.100	0.206	0.043
	2–3	0.106	0.061	0.359	0.129
	3–4	0.080	0.086	0.226	0.042
	4–5	0.089	0.117	0.366	0.126

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Table 6a. Results of the Kolmogorov-Smirnov test. Normality distributions are marked in bold. Significant differences are in bold.

Variable	Transformation	K-S p-value	Skewness	Skewness Std. Err. Skewness	Kurtosis	Kurtosis Std. Err. Kurtosis
% Chl *a* Autumn	–	< 0.10	0.953	0.403	−0.246	0.788
% Chl *a* Spring	–	> **0.20**	0.414	0.580	−1.220	1.121
% Chl *a* Trawled	–	< 0.10	1.341	0.427	0.914	0.833
% Chl *a* Untrawled	–	> **0.20**	1.161	0.524	0.364	1.014
% Chl *a* Autm trawled	–	< 0.10	0.990	0.512	−0.285	0.992
% Chl *a* Autm untrawled	–	> **0.20**	0.849	0.597	−0.537	1.154
% Chl *a* SPR trawled	–	> **0.20**	0.022	0.687	−1.741	1.334
% Chl *a* SPR untrawled	–	> **0.20**	0.477	0.913	−3.086	2.000
Chl *a* to Pheo *a* ratio Autumn	–	< 0.01	2.492	0.409	5.534	0.798
Chl *a* to Pheo *a* ratio Spring	–	> **0.20**	0.991	0.580	−0.300	1.121
Chl *a* to Pheo *a* ratio Trawled	Log $(x+1)$	< 0.05	1.248	0.427	0.166	0.833
Chl *a* to Pheo *a* ratio Untrawled	Log $(x+1)$	< 0.15	1.571	0.536	1.530	1.038
Chl *a* to Pheo *a* ratio Autm trawled	Log $(x+1)$	< 0.10	2.061	0.512	3.495	0.992
Chl *a* to Pheo *a* ratio Autm untrawled	Log $(x+1)$	< 0.20	1.924	0.597	3.657	1.154
Chl *a* to Pheo *a* ratio SPR trawled	–	> **0.20**	1.076	0.687	0.572	1.334
Chl *a* to Pheo *a* ratio SPR untrawled	–	> **0.20**	0.733	0.913	−2.262	2.000
Asp to BALA ratio Autumn	–	> **0.20**	0.963	0.434	1.326	0.845
Asp to BALA ratio Spring	–	> **0.20**	0.542	0.661	0.364	1.279
Asp to BALA ratio Trawled	–	> **0.20**	0.991	0.472	1.142	0.918
Asp to BALA ratio Untrawled	–	> **0.20**	1.623	0.564	4.587	1.091
Glu to GABA ratio Autumn	–	> **0.20**	1.324	0.448	1.702	0.872
Glu to GABA ratio Spring	–	> **0.20**	2.154	0.661	5.691	1.279
Glu to GABA ratio Trawled	–	> **0.20**	1.641	0.481	3.574	0.935
Glu to GABA ratio Untrawled	–	> **0.20**	1.176	0.580	0.800	1.121
Xylose Trawled	–	> **0.20**	0.380	0.524	−0.792	1.014
Xylose Untrawled	–	> **0.20**	1.796	0.616	3.426	1.191
Rhamnose Trawled	–	> **0.20**	0.280	0.524	0.001	1.014
Rhamnose Untrawled	–	> **0.20**	-0.137	0.616	−0.175	1.191

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Table 6b. Results of the Hartley's F_{max} test. Homogeneity of variance is marked in bold. Transformed data are marked with an asterisk. Significant differences are in bold.

Macromolecule	Differences to test	Indicator	Variance AUTM	Variance SPR	Variance TRAW	Variance UNTRAW	F-ratio	*df*	N° of groups
Pigments	Between Seasons	% Chl *a*	4.62	35.17			7.61	33	2
		Chl *a* to Pheo *a* ratio*	0.67	3.46			**5.16**	32	2
	Between Trawling Regions	% Chl *a*			23.81	6.35	3.75	29	2
		% Chl *a* SPR			44.22	13.84	**3.20**	9	2
		% Chl *a* AUTM			5.66	3.46	**1.64**	19	2
		Chl *a* to Pheo *a* ratio			0.0576	0.0625	**1.09**	29	2
		Chl *a* to Pheo *a* ratio SPR			2.47	6.00	**2.43**	9	2
		Chl *a* to Pheo *a* ratio AUTM*			0.0361	0.0225	**1.60**	19	2
Amino Acids	Between Seasons	Asp to BALA ratio	68.72	15.05			4.57	28	2
		Glu to GABA ratio	78.68	62.09			**1.27**	26	2
	Between Trawling Regions	Asp to BALA ratio			47.20	69.56	**1.47**	23	2
		Glu to GABA ratio			55.65	105.88	**1.90**	22	2
Carbohydrates	Between Trawling Regions	Xylose			0.0004	0.0049	12.25	18	2
		Rhamnose			0.0049	0.0169	3.45	18	2

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Table 6c. Results of the univariate statistical test ANOVA for pigments (Chl *a* and Chl *a* to Pheo *a* ratio) amino acids (Asp to BALA and Glu to GABA ratios) and carbohydrates (xylose and rhamnose). Significant differences are in bold.

Macromolecule	Differences to test	Indicator	Variability	SS	DF	MS	*F*	p-value
Pigments	Between Seasons	**% Chorophyll *a***	**Inter**	**179.063**	**1**	**179.063**	**13.025**	**0.001**
			Intra	**646.128**	**47**	**13.747**		
		Chl *a* to Pheo *a* ratio	**Inter**	**14.129**	**1**	**14.129**	**9.302**	**0.004**
			Intra	**69.871**	**46**	**1.519**		
	Between Trawling Regions	% Chlorophyll *a*	Inter	21.329	1	21.329	1.247	0.270
			Intra	803.862	47	17.103		
		% Chlorophyll *a* SPR	Inter	39.629	1	39.629	1.137	0.306
			Intra	453.246	13	34.865		
		% Chlorophyll *a* AUTM	Inter	0.092	1	0.092	0.019	0.890
			Intra	153.160	32	4.786		
		Chl *a* to Pheo *a* ratio	Inter	0.005	1	0.005	0.094	0.761
			Intra	2.668	46	0.058		
		Chl *a* to Pheo *a* ratio SPR	Inter	2.140	1	2.140	0.601	0.452
			Intra	46.305	13	3.562		
		Chl *a* to Pheo *a* ratio AUTM	Inter	0	1	0.000	0.006	0.937
			Intra	0.96	32	0.030		
Amino Acids	Between Seasons	Asp to BALA ratio	Inter	73.546	1	73.546	1.346	0.253
			Intra	2076.002	38	54.632		
		Glu to GABA ratio	Inter	95.214	1	95.214	1.285	0.265
			Intra	2668.108	36	74.114		
	Between Trawling Regions	Asp to BALA ratio	Inter	20.010	1	20.010	0.357	0.554
			Intra	2129.538	38	56.041		
		Glu to GABA ratio	Inter	55.323	1	55.323	0.736	0.397
			Intra	2707.999	36	75.222		
Carbohydrates	Between Trawling Regions	**Xylose**	**Inter**	**0.0156**	**1**	**0.016**	**6.040**	**0.020**
			Intra	**0.077**	**30**	**0.003**		
		Rhamnose	Inter	0.019	1	0.019	1.921	0.176
			Intra	0.297	30	0.010		

"SS" means Sum of Squares.
"DF" means Degrees of Freedom.
"MS" means Mean Squares and is obtained dividing the sum of squares by the degrees of freedom.
"*F*" represents the result of the F-Test and is obtained dividing the mean squares of the inter-group variability by the mean squares of the intra-group variability.

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Table 7. Results of the multivariate statistical test ANOSIM for pigments (Chl *a* degradation products and carotenoids), fatty acids (PUFA, MUFA, MC-FA and LC-FA) amino acids (total THAA, protein THAA and neutral THAA) and carbohydrates (sum of glucose and mannose). Significant differences are shown in bold.

Macromolecule	Differences to test	Transformation	Indicator	Global R	*P*
Pigments	Between Seasons	Square root	**% Chl *a* degradation products**	**0.212**	**0.002**
		Square root	**% Carotenoids**	**0.194**	**0.004**
	Between Trawling Regions	Square root	% Chl *a* degradation products	0.036	0.199
		Square root	% Carotenoids	-0.043	0.862
Fatty Acids	Between Seasons	Fourth root	PUFA	0.067	0.063
		Square root	**MUFA**	**0.779**	**0.001**
		Square root	MC-FA	−0.029	0.616
		Square root	**LC-FA**	**0.463**	**0.001**
	Between Trawling Regions	Fourth root	PUFA	0.018	0.198
		Square root	**MUFA**	**0.115**	**0.018**
		Square root	MC-FA	0.044	0.117
		Square root	LC-FA	0.008	0.332
		Square root	LC-FA SPR	0.104	0.183
		Square root	**LC-FA AUTM**	**0.115**	**0.013**
Amino Acids	Between Seasons	Square root	Total THAA	0.032	0.303
		Square root	Protein THAA	0.016	0.358
		Square root	Neutral THAA	0.033	0.295
	Between Trawling Regions	Square root	**Total THAA**	**0.300**	**0.001**
		Square root	**Protein THAA**	**0.318**	**0.001**
		Square root	**Neutral THAA**	**0.372**	**0.001**
Carbohydrates	Between Trawling Regions	Square root	Glucose + Mannose	−0.053	0.893

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Table 8. Results of the multivariate statistical test SIMPER carried out on those biomarkers which better evidenced differences between sampling seasons (Chl *a* and MUFA) and between trawling regions (protein and neutral THAA).

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Table 8a. Intra-group distances within the a priori-defined groups UTR, TR, SPR and AUTM.

	Intra-Group Distances			
Group	UTR	TR	SPR	AUTM
Average square distance	15.62	19.79	21.45	18.87
Variable contribution (%)	24 : 1 (6.94)	18 : 1t (5.66)	Glu (6.32)	16 : 1 (5.46)
	Asp (6.79)	His (5.37)	Ile (6.22)	Arg (5.43)
	Phe (6.64)	22 : 1 (5.32)	Leu (5.37)	Lys (5.36)
	16 : 1 (6.05)	16 : 1 (5.20)	Val (5.26)	Asp (5.25)
	22 : 1 (6.02)	18 : 1c (5.05)	18 : 1c (5.22)	Gly (5.25)
	Tyr (6.01)	18 : 1 (5.04)	Ala (5.07)	His (5.24)
	Arg (5.02)	Tyr (4.91)	His (5.04)	Ser (5.16)
	Thr (5.00)	Gly (4.75)	22 : 1 (5.00)	Ala (5.14)
	Lys (4.98)	Phe (4.40)	Ser (4.74)	Phe (5.13)
	18 : 1c (4.98)	Val (4.37)	Tyr (4.72)	Tyr (5.13)
	His (4.56)	Leu (4.28)	Arg (4.45)	Val (5.12)
	Ser (3.96)	Ser (4.11)	Phe (4.38)	Leu (5.12)
	Chl *a* (3.95)	Glu (4.09)	Gly (4.27)	Ile (4.78)
	18 : 1 (3.69)	Ile (4.05)	16:1 (4.08)	Glu (4.74)
	Glu (3.40)	24 : 1 (4.03)	Thr (3.92)	24 : 1 (4.66)
	Gly (3.20)	Ala (4.03)	Asp (3.84)	18 : 1 (4.42)
	18 : 1t (3.19)	Arg (3.97)	24 : 1 (3.71)	18 : 1t (3.77)
	Val (2.05)	Thr (3.95)	20 : 1 (3.71)	20 : 1 (3.58)
	Leu (1.82)	Lys (3.87)	Lys (3.60)	Chl *a* (3.20)
	Ile (1.69)	20 : 1 (3.67)	18 : 1t (1.94)	18 : 1c (1.72)
	Ala (1.50)	Asp (3.42)	18 : 1 (1.41)	22 : 1 (0.67)

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Table 8b. Inter-group distances between UTR and TR and between SPR and AUTM.

	Inter-Group Distances	
Groups Average square distance	UTR and TR 51.20	SPR and AUTM 51.67
Variable contribution (%)	Ala (5.42) Ile (5.37) Leu (5.22) Val (5.12) Glu (5.02) Ser (4.90) Lys (4.84) Thr (4.79) Arg (4.77) Asp (4.74) Gly (4.69) 18 : 1 (4.43) 24 : 1 (4.37) 20 : 1 (4.27) Phe (4.23) 18 : 1c (4.18) 18 : 1t (4.18) His (4.08)	22 : 1 (7.85) 18 : 1c (6.90) 18 : 1t (5.63) 20 : 1 (5.51) Chl *a* (5.22) 18 : 1 (5.15) 24 : 1 (4.57) Glu (4.10) Ile (4.08) Phe (4.06) Asp (4.04) Tyr (4.01) Lys (3.98) Ser (3.98) Gly (3.98) Ala (3.95) Val (3.93) Leu (3.92)

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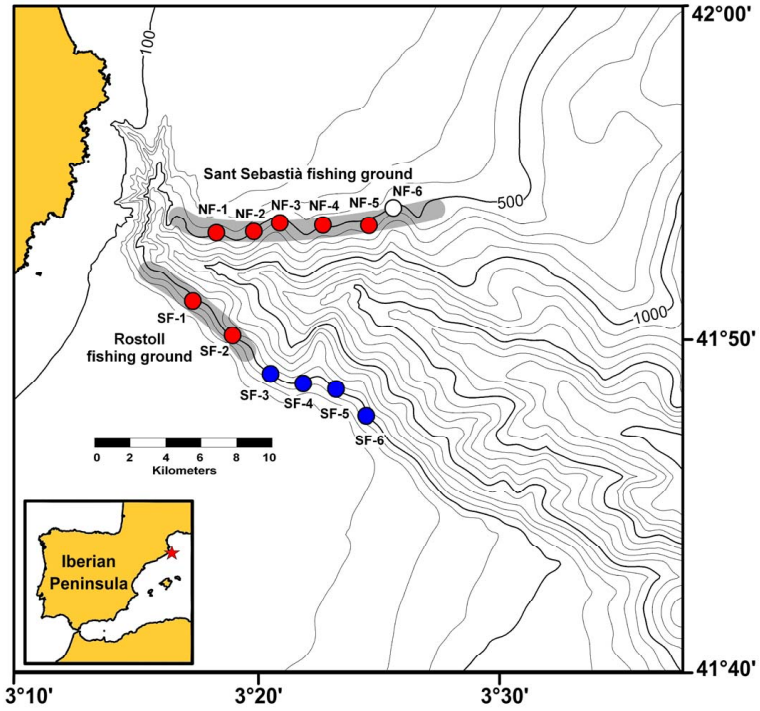

Fig. 1. Bathymetric chart of the La Fonera Canyon showing the core stations location. The main fishing grounds active on the canyon flanks are marked with grey lines. Coordinates are positive North and East. No sediment samples could be retrieved from station NF-6 due to the extreme stiffness of bottom sediments at that site (see the text for details).

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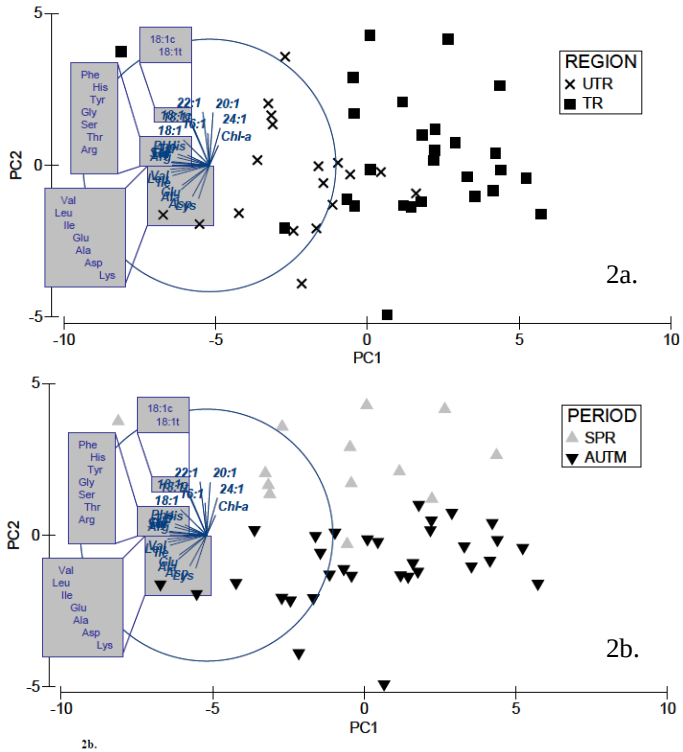

Fig. 2. Representation of the multivariate statistical test PCA carried out on those biomarkers which better evidenced differences between sampling seasons (Chl *a* and MUFA) and between trawled and untrawled regions (protein and neutral THAA). In **(a)**, stations located in the untrawled and the trawled regions are evidenced, whereas, in **(b)**, stations are distinguished based on the sampling season, spring or autumn. Biomarkers are shown in both plots (**a** and **b**).

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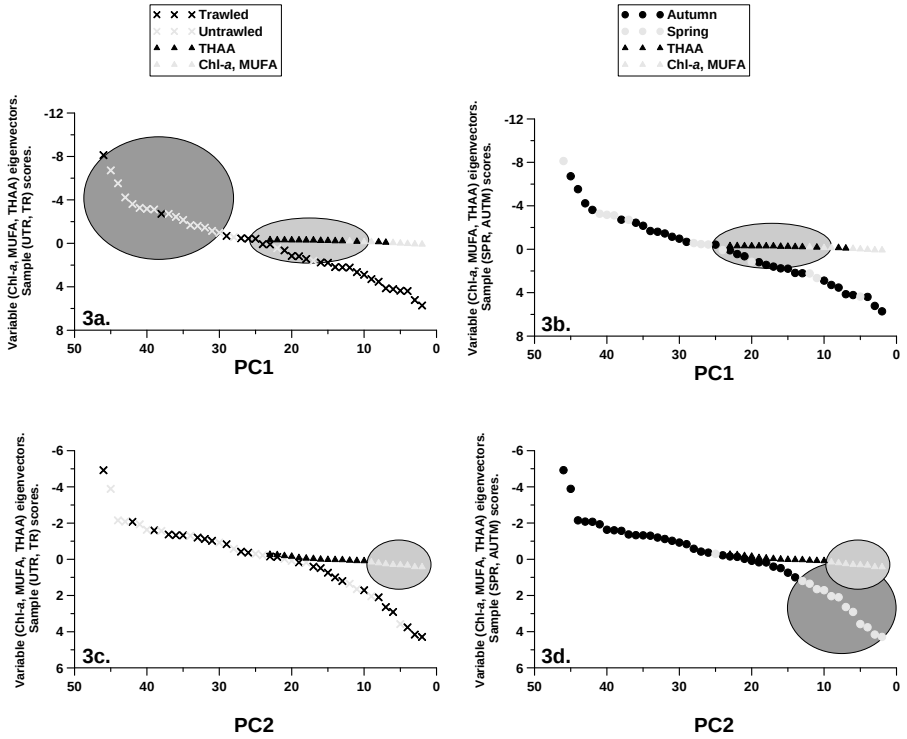

Fig. 3. PCA results. Variable (Chl *a*, MUFA, THAA) eigenvectors and sample scores for PC1 evidencing UTR and TR **(a)** and SPR and AUTM **(b)**. Variable (Chl *a*, MUFA, THAA) eigenvectors and sample scores for PC2 evidencing UTR and TR **(c)** and SPR and AUTM **(d)**.

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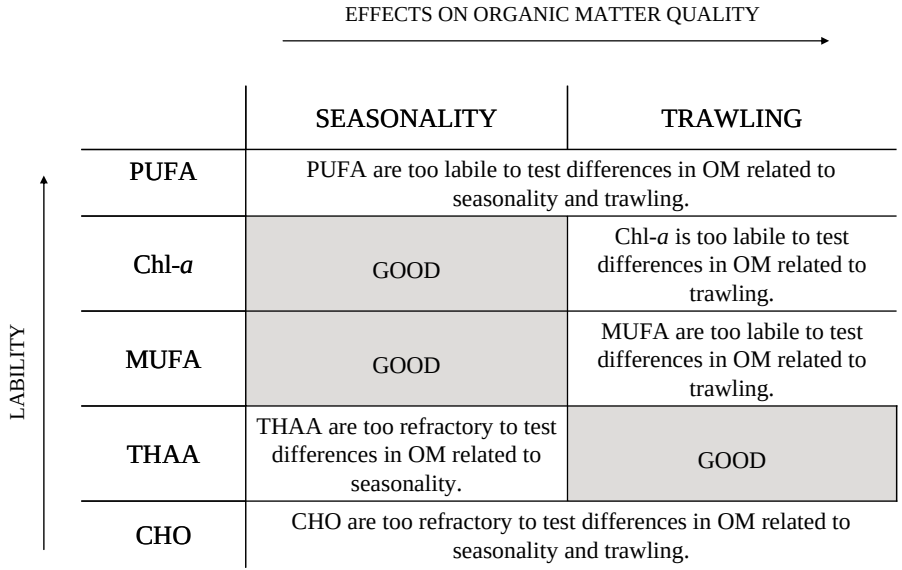

Fig. 4. Schematic representation of the results obtained in this study by using a pool of biomarkers with different labilities to investigate on the effects of seasonality and sediment reworking by trawling on the quality of the OM.

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